DEVELOPMENT OF AN INNOVATIVE APPROACH TO ASSESS THE ECOLOGICAL IMPACT OF PEATLAND DEVELOPMENT

ECOLOGICAL BACKGROUND AND PRELIMINARY MODEL DEVELOPMENT

A Report for:

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EXECUTIVE SUMMARY

With the establishment of an interagency Peat Forum in 1982, the Canadian government expressed a formal commitment to investigate the potential of peat as an alternative energy resource. Program objectives include identification of environmental impacts which may arise from peat mining, and development of mitigative measures where necessary. This report is designed to contribute to the development of environmental guidelines. The study approach is based on the premise that, in order to evaluate the significance of potential environmental impacts, the structure and function of the peatland ecosystem must be understood. Study objectives include:

- o description of key physico-chemical and biological components of peatland ecosystems;
- o identification of the types of environmental disturbances which may arise from wet and dry peat mining processes; and
- o evaluation of the sensitivity of peatland ecosystems to such disturbances.

In Part I of the report, key components of peatland ecosystems are described. These include:

- o hydrology
- o vegetation
- o physical properties of peat
- o peat chemistry
- o water chemistry
- o aquatic ecology

Relevant concepts from multidisciplinary literature sources, including soil science, hydrogeology, ecology, aquatic chemistry and lake ecosystem modelling are employed to fill in gaps where direct knowledge of peatland ecosystems is lacking. In Part II, preliminary quantitative models are developed to simulate natural and disturbed conditions, based on master variables and interactions defined in Part I. Model output is oriented toward the description of aquatic impacts.

Key elements of the report are summarized in the following sections.

Hydrology

Hydrology is characterized through a mass balance equation which describes water inputs and losses, and from which the amount of water stored in the peatland may be calculated. Major components of the water balance equation include:

- o precipitation (P)
- o ground or surface water inflow (I)
- o evaporation (E)
- o discharge (D)
- o storage (S)

Peatlands are characterized by groundwater levels which are at or near the surface for much of the year. The zone of hydrological activity (acrotelm) is defined by the maximum depth of the water table. Short-term storage capacity and discharge volumes are determined by the water table level. The main water storage compartment is the inactive layer, or catotelm. This zone is permanently waterlogged and hydraulic exchange rates are low.

Northern temperate peatlands exhibit characteristic seasonal fluctuations in runoff volume which are related to precipitation distribution. In peatlands which freeze during the winter, two-thirds of annual runoff typically occurs during spring thaw. In systems which do not freeze, winter runoff patterns follow precipitation trends. During the summer months, evaporation reduces runoff and, in some systems, outflow may cease altogether.

Vegetation

Peatland vegetation is the precursor of peat. Thus, knowledge of the factors which affect species composition, growth and decomposition is essential in the determination of peat accumulation rates and physico-chemical properties, nutrient and trace element fluxes. Peatland classifications are often based on vegetational species composition, since plants are sensitive ecological indicators of climatic and hydrodynamic conditions. Succes ional scenarios are preserved in the peat stratigraphy.

In northern latitudes, peat accumulation rates are a function of the amount of plant material produced (as defined by net primary productivity and standing crop) and the rate

at which it decomposes. Accumulation is favoured by the waterlogged, anoxic, nutrient poor conditions, commonly encountered in bogs. Plant decomposition also results in the release of nutrients and trace elements into solution. These may, in turn, be complexed with the peat taken up by living plants or leach from the system.

Peatlands, and especially bogs, have traditionally been considered to be nutrient-poor. However, while total nutrient concentrations in peatlands may often be lower than those of mineral soils, it appears that bioavailability rather than supply may limit growth. Nitrogen and phosphorus are contained largely in organic compounds. Biologically-mediated mineralization to inorganic (bioavailable forms) is tightly controlled by oxygen supply and acidic conditions.

Plant decomposition in ombrotrophic systems may also introduce trace contaminants into the soil solution. Sphagnum and other bog species have been shown to accumulate heavy metals introduced by atmospheric deposition.

Physical Properties of Peat

Classifications of peat for commercial uses are generally based on physical characteristics, since these determine water retention capacity and hydraulic conductivity. Most commonly measured physical properties (i.e., bulk density, von Post scale, fibre content) are indicators of decompositional state and, as a result, all are statistically intercorrelated.

Peat exhibits a wide range in hydraulic conductivity (10^{-9} cm/sec - 8 cm/sec). This can be related to differences in botanical origin and decompositional state, depth within the profile and compaction. The highest conductivities are exhibited in poorly decomposed Sphagnum peats. Conversely, water retention capacity is highest in well-humified peats, with small pore spaces.

Chemistry

The peat-pore water complex is highly chemically reactive. It is influenced by the amount and source of water input and, in turn, determines the quality of the discharge waters. Significant differences are observed between the peat and water chemistry of

ombrotrophic and minerotrophic systems. Bogs characteristically exhibit higher concentrations of acidity-related parameters such as (acidity), colour, humic and fulvic acids, trace metals and low pH. Fens exhibit higher concentrations of parameters which reflect telluric influence; calcium, magnesium, alkalinity, and electrical conductivity, and slightly acidic to circumneutral pH.

The acidity of ombrotrophic systems has a major influence or discharge water quality. Recent studies suggest that low pH's are maintained largely through the dissociation kinetics of weak organic acids. Trace metals are solubilized under acidic conditions. Most peat profiles show sharp drops in metal concentrations below the zone of water table fluctuation. The resistance of organic-dominated systems to pH changes as a result of mineral acid input through acid rain has received little study.

Aquatic Ecology

Peatlands discharge waters may enter the drainage system through streams, rivers, lakes or estuaries. The potential impact of peatland drainage and mining activities on downstream aquatic communities is perceived to be a major environmental concern. However, at the present time, the influence of natural peatland discharge on aquatic biota is poorly understood. Many economically important fish species occur in "brown-water" systems, which receive large volumes of peatland discharge. However, there is evidence to suggest that humic substances may exert a toxic effect on certain species. In addition, the available data indicate that undisturbed peatland discharge waters commonly do not conform to Federal Water Quality Objectives for the Protection of Aquatic Life for parameters such as pH, dissolved oxygen, nutrients and metals. This area of peatland ecology represents a major information gap which must be resolved before the impacts of peatland development can be accurately assessed.

Mining Impacts

The literature suggests that potential aquatic impacts arising from peatland development relate to alteration of the hydrological regime and impairment of water quality, with subsequent direct or indirect effects on aquatic biota. Currently, too few field observations have been conducted to accurately assess the magnitude or duration of impacts. Nonetheless, based on field observations and ecological reasoning, the following tentative conclusions as to the types of impacts which may occur can be made.

Hydrology

- o Wet mining would appear to be less disruptive to the hydrologic regime than dry mining.
- o Vegetation removal and drainage significantly alter the water balance of the system by causing a net decrease in evaporation and alteration of storage capacity.
- o Increased or decreased runoff may be associated with peatland drainage.
- o Peatland drainage alters stormflow response; generally decreasing by time and increasing peak runoff rates.
- o Hydrologic impacts arising from wet mining will relate primarily to the presence or absence of an outflow, and the nature of the receiving environment.

Water Quality

- o In the absence of a treatment facility, peatland drainage is likely to increase the concentrations of suspended and dissolved solids and other related parameters such as turbidity, dissolved oxygen, etc.
- o Alterations in pH and other acidity-related parameters will depend on the influence of mineral-enriched groundwater and the depth of ditches. If ditches are dug to the zone of influence of the mineral layer, pH may increase.
- o Water quality impacts arising from wet mining will depend on the water quality of the dredge ponds the method of release and the nature of the receiving environment.
- o Preliminary studies indicate that ponds which are dredged to the mineral layer have significantly different water quality than peat-bottomed ponds.

Modelling

The preliminary model contains hydrology, biogeochemistry and toxicity subcomponents. Analyses contained in this report include:

- o a description of the model framework, including ultimate goals, major assumptions, rationale for choice of input parameters, and model limitations;

- o development of a preliminary hydrology model;
- o analysis of water balance in an undisturbed bog and alterations produced by wet and dry mining;
- o conceptual models for pH, major cations, carbon, nutrients, heavy metals, oxygen and redox potential;
- o simulations of peat accumulation processes and electroneutrality balances (pH) in an undisturbed bog; and
- o simulation of water chemistry of outflow from a bog subjected to dry mining. Parameters considered include pH, nutrients, metals and toxicity.

Based on these analyses, a number of preliminary results can be derived.

The following are viewed as the master variables for the model:

- o the flow pathway and the rate of water flow,
- o pH,
- o the redox potential (Eh or pE),
- o the bulk density and decay rate of the peat,
- o adsorption properties of peat,
- o soluble organics, and
- o chemical precipitates.

Hydrology

- o Wet mining of an ombrotrophic bog would not substantially alter the hydrological pathways of a bog, while dry mining would induce a larger proportion of rainfall to leave via runoff.

- o Simulation of the monthly height of the water table using the dynamic water balance equation shows reasonable agreement with published data.

- o Both hydraulic conductivity and vertical piezometric gradient should be measured to assess the significance of vertical transport in anaerobic bog waters.

Geochemistry

- The fulvic acid system and chemical electroneutrality are used to model the pH of anaerobic ombrotrophic bog waters. This system appears to be adequate to described observations upon undisturbed bogs where the pH 4.0. If the bog is disturbed (i.e., dry mining), the modelling analyses suggest that the oxidation of ammonia (and other reduced species) and the production rate of humic substances have a critical effect upon the calculated pH in the outflow. In the case of dry mining, the inorganic carbon buffering system and the effects of pH upon the pK of fulvic acid must be included in the model to adequately predict pH increases above pH 5.

- Oxygen consumption and denitrification are used to estimate the significant zones of redox change in the peatland. Calculations presented in the report assume that methane transport from anaerobic layers can explain oxygen consumption rates. Other sources of oxygen consumption (POC, nitrification) will be considered in the future.

- Ionic, organic and particulate phases of metals are the main forms used in the model. For Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{2+} and Al^{3+}, it is assumed that adsorbed forms are the main particulate phase. For other divalent metals (e.g., Ca^{2+}, Mn^{2+}, Cd^{2+}), it is assumed that a metal sulphide precipitate is the main form in anaerobic saturated zones.

- The desorption rate of adsorbed metals and the dissolution rate of precipitates, together with the hydrological pathway are the critical parameters influencing metal concentrations in the bog effluent under dry mining conditions. The calculated concentrations range over two orders of magnitude given plausible estimates for these parameters. The calculated concentrations generally bracket water quality standards (higher and lower), indicating the need for more accurate measurements (desorption rate, dissolution rate).

Toxicity

- Calculations are presented which demonstrate how fulvic acid-metal complexation decrease metal toxicity.

RECOMMENDATIONS FOR FUTURE WORK

Future studies should concentrate in two general areas:

- filling in information gaps in our understanding of peatland ecology; and
- model refinement, calibration and verification; and

Peatland Ecology

Many dynamic properties of peatland ecosystems are poorly understood. Consequently, there are inconsistencies in the literature data which may be the result of natural variability, experimental error, or inadequate baseline data. Major components requiring further study include:

- integrated data collection;
- quantitative studies of hydrological regime;
- aspects of the behaviour of organic acids produced by peat decomposition including:
  - buffering capacity - influence of acid rain,
  - kinetics of metal sorption and release under varying reduction - oxidation conditions and pH, and
  - aquatic toxicity of humic and fulvic acids;
- development of acid - resistant strains of aquatic biota.

Modelling

A major field study to collect a complete set of site-specific data from which model calibration can be derived is required. This should be augmented by <u>in situ</u> and controlled laboratory experiments where necessary.

Model refinements may include the following:

- o present efforts have neglected the effects of plant growth upon biochemical transformations;
- o more steady-state modelling calculations will be made in the future to complete the test set of data;
- o coding will be completed. The effects of vegetation growth need to be included in order to calibrate the model for an existing peatland and in order to provide confidence in using it to assess the effects of mining upon existing peatlands (which are actively growing); and
- o a finite difference model, which consideres up to eight layers of different permeability, has been coded, but not debugged for the generic peatland. The model will be refined and results incorporated into the hydrology model and into hydrological pathways of the biogeochemical model.

RÉSUMÉ ADMINISTRATIF

En 1982, au cours de la table ronde inter-organismes sur la tourbe, le gouvernement du Canada s'est formellement engagé à envisager l'utilisation de la tourbe comme énergie de remplacement. Le programme adapté vise, entre autres, à identifier les répercussions environnementales, de l'exploitation de la tourbe et à mettre au point les mesures d'atténuation nécessaires. Le présent rapport a pour but d'aider à l'élaboration des directives environnementales. L'étude est basée sur les prémisses qu'il faut d'abord comprendre la structure et le fonctionnement de l'écosystème des tourbières avant de pouvoir évaluer les répercussions environnementales éventuelles de leur exploitation. L'étude a notamment pour objectif,

- de décrire les principaux éléments physico-chimiques et biologiques de l'écosystème des tourbières;
- d'identifier le genre de perturbations environnementales pouvant résulter de l'exploitation de la tourbe par voie sèche et par voie humide; et
- d'évaluer la sensibilité des écosystèmes de tourbière à ces perturbations

Dans la première partie du rapport, on décrit les principaux éléments des écosystèmes de tourbière, soit:

- hydrologie
- végétation
- propriétés physiques de la tourbe
- chimie de la tourbe
- chimie de l'eau
- écologie aquatique

En l'absence de renseignements traitant directement de la tourbe, on les a remplacé par des concepts pertinents tirés de sources documentaires spécialisées dans plusieurs disciplines, par exemple la pédologie, l'hydrogéologie, l'écologie, la chimie de l'eau et la modélisation des écosystèmes lacustres. Dans la deuxième partie, on met au point des ébauches de modèle quantitatif permettant de simuler des conditions naturelles et des

perturbations à partir des variables principales et des interactions définies dans la première partie. Le modèle vise à décrire les répercussions de l'exploitation des tourbières sur le milieu aquatique.

Les éléments clés du rapport sont résumés dans les sections suivants.

Hydrologie

L'hydrologie des tourbières se caractérise par une équation décrivant le bilan massique des apports et des pertes d'eau et permettant de calculer la quantité d'eau retenue par la tourbière. Voici les principales composantes de l'équation du bilan hydrologique:

- o précipitations (P)
- o apport d'eau souterrain ou superficielle (I)
- o évaporation (E)
- o débit
- o retenue (S)

Les tourbières sont caractérisées par un nappe phréatique située à la surface ou presque pendant la majeure partie de l'année. La zone d'activité hydrologique (acrotelme) est définie par la profondeur maximale de la surface de saturation. Les capacités de débit et de retenue à court terme sont déterminées par le niveau de la surface de saturation. L'eau est principalement retenue par la couche inactive ou catotelme. Cette zone est saturée d'eau en permanence et les taux d'échange hydrauliques sont faibles.

Dans les tourbières tempérées boréales, on observe des fluctuations saisonnaiaires caractéristiques du volume de ruissellement qui sont liées à la distribution des précipitations. Dans les tourbières où il y a gel pendant l'hiver, les deux tiers du ruissellement annuel se produisent généralement pendant le dégel printannier. Dans les systèmes qui ne gèlent pas, le ruissellement hivernal correspond aux précipitations. Pendant les mois d'été, l'évaporation réduit le ruissellement et, dans certains systèmes, l'eau peut même s'arrêter complètement de couler.

Végétation

La végétation de tourbière est le précurseur de la tourbe. Il est donc essentiel pour déterminer les taux d'accumulation de la tourbe et les variations des propriétés physico-chimiques et des teneurs en sels nutritifs et en éléments traces de connaître les facteurs modifiant la composition des espèces ainsi que leur croissance et leur décomposition. Les classifications des tourbières se basent souvent sur la composition des espèces végétales car les plantes sont des indicateurs écologiques sensibles des conditions climatiques et hydrodynamiques. L'historique de la tourbière apparaît dans la stratigraphie de la tourbe.

Dans les régions boréales, le taux d'accumulation de la tourbe est fonction de la quantité de matières végétales produites (définie par la productivité primaire nette et la population sur pied) et de son taux de décomposition. L'accumulation est favorisée par les conditions régnant en général dans les tourbières oligotrophes, soit la saturation en eau, l'anoxie et la pauvreté en éléments nutritifs. La décomposition des plantes provoque la libération de sels nutritifs et d'éléments traces dans la solution. Ces derniers peuvent ensuite former un complexe avec la tourbe, être absorbés par les plantes vivantes ou entraînés hors du système.

On a traditionnellement considéré que les tourbières, spécialement les tourbières oligotrophes, sont pauvres en sels nutritifs. Toutefois, bien que les concentrations totales des tourbières en sels nutritifs soient souvent inférieures à celles des sols minéraux, il appert que c'est la bioaccessibilité et non pas la quantité présente qui limite la croissance. L'azote et le phosphore font partie la plupart du temps de composés organiques. La minéralisation biologique de ces composés en composés inorganiques (formes bioaccessibles) est réglée par l'apport en oxygène et des conditions acides.

La décomposition des plantes des systèmes ombrotrophes peut aussi introduire des contaminants traces dans la solution de sol. On a montré que

le sphaigne et les autres espèces des tourbières oligotrophes accumulent les métaux lourds provenant des dépôts atmosphériques.

Propriétés physiques de la tourbe

Pour un usage commercial, la tourbe est en général classée d'après ses caractéristiques physiques qui en déterminent la capacité de rétention d'eau et la conductivité hydraulique. Les propriétés physiques faisant le plus souvent l'objet de mesures (p. ex., densité apparente, échelle von Post, teneur en fibre) sont des indicateurs de l'état de décomposition et y sont donc toutes inter-reliées statistiquement.

Le coefficient de Darcy de la tourbe varie sur une vaste plage (10^{-9} cm/s - 8 cm/s. Ce fait peut être lié à ses différentes origines botaniques, à ses différents états de décomposition, à sa profondeur dans le profil et à la compression subie. On trouve les coefficients les plus grands dans les tourbes de sphaigne peu décomposées. Par contre, la capacité de rétention d'eau est supérieure pour les tourbes bien humifiées ayant de petits espaces lacunaires.

Chimie

Le complexe tourbe-eau de porosité réagit beaucoup chimiquement. Sa qualité est fonction de la quantité et de l'origine de l'apport d'eau et, par conséquent, détermine la qualité des eaux de décharge. On observe des différences importantes entre la chimie tourbe-eau des systèmes ombrotrophes et minérotrophes. Les tourbières oligotrophes ont des propriétés caractéristiques des milieux acides: faible pH, forte coloration, fortes teneurs en acides humique et fulvique et en métaux traces. Les propriétés des tourbières oligotrophes reflètent davantage l'influence tellurique qui s'est exercée pendant leur formation: fortes concentrations en calcium et en magnésium, alcalinité élevée, grande conductivité et un pH légèrement acide ou à peu près neutre.

L'acidité des systèmes ombrotrophes a une influence importante sur la qualité des eaux de décharge. Des études récentes laissent supposer que le

pH demeure bas en grande partie à cause de la dissociation cinétique d'acides organiques faibles. En conditions acides, les métaux traces se solubilisent. Dans le profil de la plupart des tourbes, on observe une brusque baisse de la concentration en métaux ou de la zone de fluctuation de la surface de saturation. On a peu étudié la résistance des systèmes formés en majeure partie de composés organiques aux variations de pH par suite de l'arrivée d'acides minéraux sous forme de pluies acides.

Écologie aquatique

Les eaux de décharge des tourbières peuvent pénétrer dans les bassins versants par l'intermédiaire des ruisseaux, des rivières, des lacs ou des estuaires. Les répercussions éventuelles du drainage et de l'exploitation d'une tourbière sur les communautés aquatiques d'aval apparaissent comme un sujet important d'inquiétude concernant le milieu. Cependant, on comprend mal présentement l'influence de la décharge naturelle des tourbières sur le biote aquatique. Beaucoup d'espèces économiquement importantes de poissons vivent dans les "eaux brunes" où de grands volumes l'eau de tourbières se déchargent. Cependant, des observations laissent entendre que les matières humiques peuvent avoir un effet toxique sur certaines espèces. De plus, les données existantes montrent que les eaux de décharge des tourbières intactes ne sont, en général, pas conformes aux objectifs de qualité des eaux fixés par le gouvernement fédéral pour la protection de la vie aquatique en ce qui concerne des paramètres comme le pH, les teneurs en oxygène dissous, en sels nutritifs et en métaux. Il y a, dans ce domaine de l'écologie de tourbières, en manque important dans les connaissances qui doit être comblé avant que les répercussions de l'exploitation des tourbières puissent être évaluées de façon précise.

Répercussions de l'exploitation

La littérature laisse entendre que les répercussions potentielles de l'exploitation des tourbières sur le milieu aquatique sont reliées à la modification du régime des eaux et à l'appauvrissement de la qualité de l'eau

qui ont des effets directs ou indirects sur le biote aquatique. On a actuellement effectué trop peu d'observations au champ pour pouvoir évaluer de façon précise l'importance ou la durée des répercussions. Néanmoins, en se basant sur les observations existantes et en raisonnant à la façon d'un écologiste, il est possible de tirer les conclusions provisoires qui suivent quant au type de répercussions attendues:

Hydrologie

- L'exploitation par voie humide semble moins bouleverser le régime des eaux que l'exploitation par voie sèche.
- L'élimination de la végétation et le drainage modifient beaucoup le bilan hydrologique d'un système en provoquant une diminution nette de l'évaporation et en modifiant la capacité de rétention.
- Le drainage des tourbières peut provoquer une augmentation ou une diminution du ruissellement.
- Le drainage d'une tourbière change son débit d'orage; en général, temps sèchement diminue et le débit de pointe de ruissellement augmente.
- Les répercussions hydrologiques d'une exploitation minière par voie humide dépendent surtout de la présence ou de l'absence d'une décharge ainsi que de la nature du milieu récepteur.

Qualité de l'eau

- En l'absence d'une usine de traitement des eaux, il est probable que le drainage d'une tourbière fasse augmenter les concentrations en matières solides en suspension et en solution ainsi que les paramètres qui s'y rapportent, soit la turbidité, l'oxygène dissous, etc.
- Les variations de pH et des paramètres reliés à l'acidité dépendent de l'influence des eaux souterraines riches en sels minéraux et de la profondeur des fossés. Lorsque ceux-ci sont creusés jusqu'à la zone d'influence de la couche minérale, le pH peut augmenter.
- Les répercussions de l'exploitation par voie humide sur la qualité des eaux dépendent de la qualité des eaux des étangs de dragage, du mode de rejet des equx et de la nature du milieu récepteur.

- Des études préliminaires montrent que la qualité des eaux des étangs dragués jusqu'à la couche minérale est nettement différente de celle des étangs à fond de tourbe.

Modélisation

Le modèle préliminaire fait intervenir des sous-composantes hydrologiques, biogéochimiques et toxicologiques. Les études faisant l'objet du présent rapport comprennent entre autres:

- description du cadre d'application du modèle, y compris le but ultime, les principales hypothèses, l'explication du choix des paramètres d'entrée et les limitations du modèle;
- mise au point d'un modèle hydrologique préliminaire;
- étude du bilan hydrologique dans une tourbière oligotrophe intacte et des altérations provoquées par l'exploitation par voie humide ou sèche;
- conception de modèles tenant compte du pH, des teneurs en cations principaux, en carbone, en sels nutritifs, en métaux lourds et en oxygène dissous, et du potentiel d'oxydoréduction;
- simulation des processus d'accumulation de la tourbe et des bilans à pH neutre dans une tourbière oligotrophe intacte; et
- simulation de la chimie de l'eau de décharge d'une tourbière oligotrophe soumise à l'exploitation par voie sèche. Les paramètres envisagés sont, entre autres, le pH, les teneurs en sels nutritifs et en métaux et la toxicité.

Ces études permettront d'extrapoler un certain nombre de résultats préliminaires.

Les variables les plus importantes dans la modélisation sont les suivantes:

- trajet et débit du cours d'eau,
- pH,

- potentiel d'oxydoréduction (Eh ou pE),
- densité apparente et taux de décomposition de la tourbe,
- adsorptivité de la tourbe,
- substances organiques solubles et
- précipités chimiques.

Hydrologie

- L'exploitation d'une tourbière ombrotrophe par voie humide ne modifierait pas de façon importante les voies d'élimination de l'eau, alors que l'exploitation par voie sèche pourrait provoquer un accroissement de la proportion de ruissellement à la suite de pluies.
- La simulation de la profondeur mensuelle de la surface de saturation à l'aide de l'équation du bilan hydrologique dynamique permet d'obtenir des résultats assez conformes aux données publiées.
- Il faudrait mesurer le coefficient de Darcy et le gradient piézométrique à la verticale pour évaluer l'importance du transport à la verticale dans les eaux anaérobies des tourbières oligotrophes.

Géochimie

- Pour modéliser le pH des eaux anaérobies d'une tourbière oligotrophe ombrotrophe, on suppose un système chimiquement neutre renfermant de l'acide fulvique. Ce système semble décrire adéquatement les observations faites dans les tourbières oligotrophes intactes dont le pH est $<4,0$. Lorsque la tourbière est perturbée (p. ex., exploitation par voie sèche), les études du modèle laissent supposer que l'oxydation de l'ammoniaque (et des autres espèces réduites) et la vitesse de formation des substances humiques ont un effet critique sur le pH calculé de la décharge. Dans le cas de l'exploitation par voie sèche, il faut incorporer au modèle le tampon de carbone inorganique ainsi que les effets du pH sur la dissociation de l'acide fulvique si l'on veut prévoir de façon précise les augmentations de pH au-dessus de pH 5.
- La consommation d'oxygène et la dénitrification servent à évaluer les zones importantes de modification du potentiel d'oxydoréduction dans la

tourbière. Les calculs apparaissant dans le présent rapport sont basés sur l'hypothèse que le transport de méthane depuis les couches anaérobies peut expliquer les taux de consommation d'oxygène. À l'avenir, on tiendra compte d'autres formes de consommation d'oxygène (consommation de permanganate, dénitrification).

- Les principales formes que le modèle prévoit pour les métaux sont les formes ioniques, organiques et particulaires. Dans le cas de Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{2+} et Al^{3+}, on suppose que la forme adsorbée constitue la principale forme particulaire. Pour ce qui est des autres métaux bivalents (p. ex., Ca^{2+}, Mn^{2+}, Cd^{2+}), on suppose qu'un précipité de sulfure métallique est la principale forme dans les zones anaérobies saturées.
- Le taux de désorption des métaux et le taux de dissolution des précipités, ainsi que les voies hydrologiques sont les paramètres critiques influant sur la concentration de métaux dans les effluents de tourbières oligotrophes exploitées par voie sèche. D'après des valeurs estimatives plausibles de ces paramètres, les concentrations calculées s'étaient sur deux ordres de grandeur. Elles encadrent en général les valeurs prévues (supérieures et inférieures) par les normes de qualité de l'eau, ce qui indique la nécessité de mesures plus précides (taux de désorption, taux de dissolution).

Toxicité

- On présente des calculs démontrant comment la formation d'un complexe acide fulvique-métal diminue la toxicité de ce dernier.

RECOMMANDATIONS EN VUE DES TRAVAUX FUTURS

Les futures études devraient se concentrer sur deux domaines généraux:

- combler nos manques de connaissance de l'écologie des tourbières; et
- améliorer, étalonner et vérifier le modèle.

Écologie des tourbières

Beaucoup des propriétés dynamiques des écosystèmes de tourbières sont mal comprises. Il s'ensuit une incohérence des données rapportées dans la littérature qui peut venir de la variabilité naturelle des paramètres, d'erreurs expérimentales ou de données de base inadéquates. Parmi les composantes principales à étudier plus à fond, citons:

- collecte intégrée des données;
- études quantitatives du régime des eaux;
- comportement des acides organiques produits par la décomposition de la tourbe, entre autres:
  - pouvoir tampon - influence des pluies acides,
  - cinétique de sorption des métaux dans diverses conditions réductrices et oxydantes et à divers pH, et
  - toxicité des acides humique et fulvique dans l'eau;
- développement de souches résistantes à l'acide dans le biote aquatique.

Modélisation

Il est nécessaire qu'on effectue une étude importante sur le terrain de façon à collecter un ensemble complet de données spécifiques à chaque station qui permettront d'étalonner le modèle. Lorsque c'est nécessaire, l'ensemble peut être complété par des expériences in situ et des expériences de laboratoires témoins.

Possibilités de perfectionnement du modèle:

- les efforts actuels ne tiennent pas compte des effets de la croissance végétale sur les transformations biochemiques;
- à l'avenir, on fera davantage de calculs de modélisation à l'état stationnaire pour compléter l'ensemble de données mis à l'essai;
- le codage sera complété. Les effets de la croissance végétale doivent être inclus dans le modèle si on veut l'appliquer à une

tourbière réelle et s'en servir avec confiance pour évaluer les effets de l'exploitation des tourbières (qui augmente rapidement); et

- on a fait, pour une tourbière type, le codage d'un modèle incorporant des différences finies, qui tient compte de huit couches de perméabilité différentes mais on n'en a pas éliminé les imperfections. Le modèle sera amélioré et les résultats, incorporés dans le modèle hydrologique et dans les voies hydrologiques du modèle biogéochimique.

1

Ecological Background

1.0 INTRODUCTION

1.1 Study Rationale

Perhaps because of Canada's wealth of natural resources, the economic potential of peat has, until recently, been largely overlooked. However, peatlands cover approximately 16% of Canada's total land surface, and while much of this area lies in the remote north, peat deposits of potential economic significance are found throughout the country (Figure 1). Traditionally, peat utilization in Canada has been limited to horticultural peat (peat moss) mining with most operations concentrated in eastern Canada (Figure 2). However, in 1982, the federal government began a five-year program to investigate the potential of peat as an alternative energy resource. This initiative has stimulated widespread interest throughout the public and private sectors in all aspects of peat utilization. Consequently, it is feasible that within the next decade, large-scale mining of peat for fuel, horticulture, industrial chemicals and other products may occur in various parts of the country.

Experience in Canada and elsewhere has shown that, if environmental assessment guidelines are not developed for natural resource-based industries, major environmental issues, based on real or publicly perceived impacts, may arise. Unlike other fuels or base metals which are extracted by mining, peat is an integral part of the living ecosystem. Thus, in order to accurately evaluate impacts which may arise as a result of peat mining, it is first necessary to understand how the peatland ecosystem functions. While certain aspects of peatland ecology, such as vegetational composition and community succession, have been extensively studied, factors affecting many key variables and interactions between physico-chemical and biological processes are generally poorly understood. Consequently, there are many inconsistencies and information gaps which must be resolved before accurate predictions of potential impacts arising from mining can be made. This report utilizes multidisciplinary literature sources to provide an overview of peatland ecosystem structure and function and sensitivity to disturbance.

Key variables are incorporated into a preliminary modelling framework. Model subcomponents include hydrology, geochemistry and toxicity, and "first cut" predictions of impacts arising from wet and dry mining are made. While the study is primarily directed toward the energy peat mining industry, many of the results and conclusions apply to other forms of peat utilization.

directed toward the energy peat mining industry, many of the results and conclusions apply to other forms of peat utilization.

1.2 Specific Objectives

The specific objectives of the study are:

- o to identify key physical, chemical and biological parameters which define peatland ecosystems;
- o to characterize the variability of these parameters with respect to peatland type, geographic location and seasonal patterns;
- o to elucidate ecological interactions and interdependencies;
- o to develop a preliminary set of mathematical equations (models) which describe hydrological and biogeochemical processes for a generic peatland;
- o to identify and evaluate the significance of potential environmental impacts which may arise from peat mining;
- o to mathematically simulate a typical development scenario(s) through manipulation of key variables.

1.3 Peatland Classification and Definitions

In Canada peatlands are generally defined as areas containing accumulations of more than 40 cm of (predominantly) organic matter (Zoltai and Pollett, 1983). This is comparable to Stanek's (1977) definition of muskeg as peat accumulations of 30 cm or deeper when drained, or 45 cm undrained, and Clymo's (1983) arbitrary minimum of 30 cm. Further subdivisions such as bog, fen and swamp are defined on the basis of plant species composition and richness.

Development of North American peatland classification systems has been influenced by European researchers including Moss (1953), Sjors (1961), and Damman (1977). Other important contributions have stemmed from the earlier work of Heinselman (1963, 1970), in Minnesota, and more recently, Jeglum et al. (1974), Zoltai et al. (1973) and Zoltai and Pollett (1983). Some of the major features of the Canadian classification schemes that have resulted are presented in Table 1 and Figure 3.

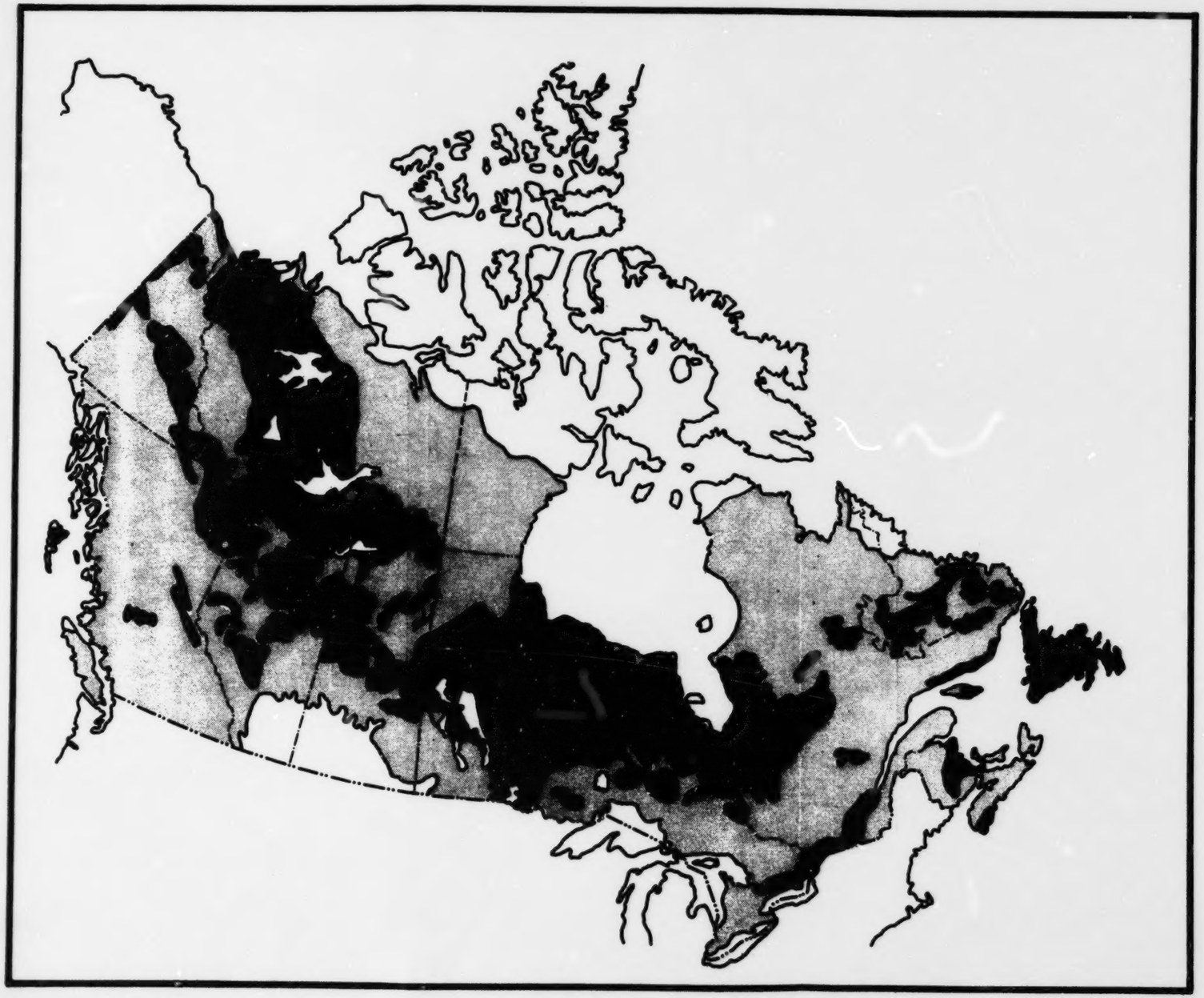


Figure 1

Peatland Resources of Canada (after Tarnocai, 1984)

Legend

Percentage of Areas Covered by Peatlands

- 0–1%
- 2–5%
- 6–25%
- 26–75%
- 76–100%

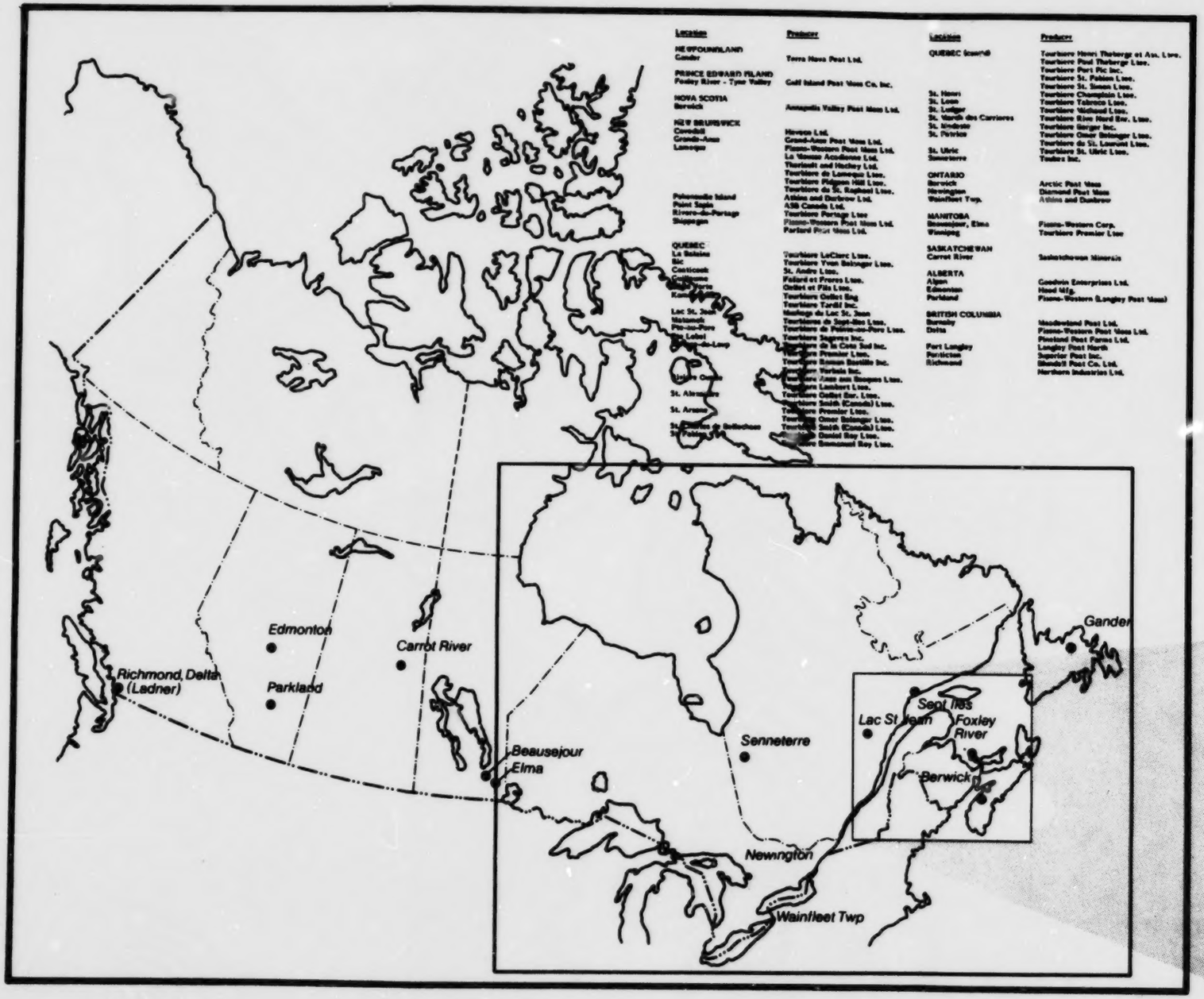


Figure 2

Locations of Peat Producers in Canada

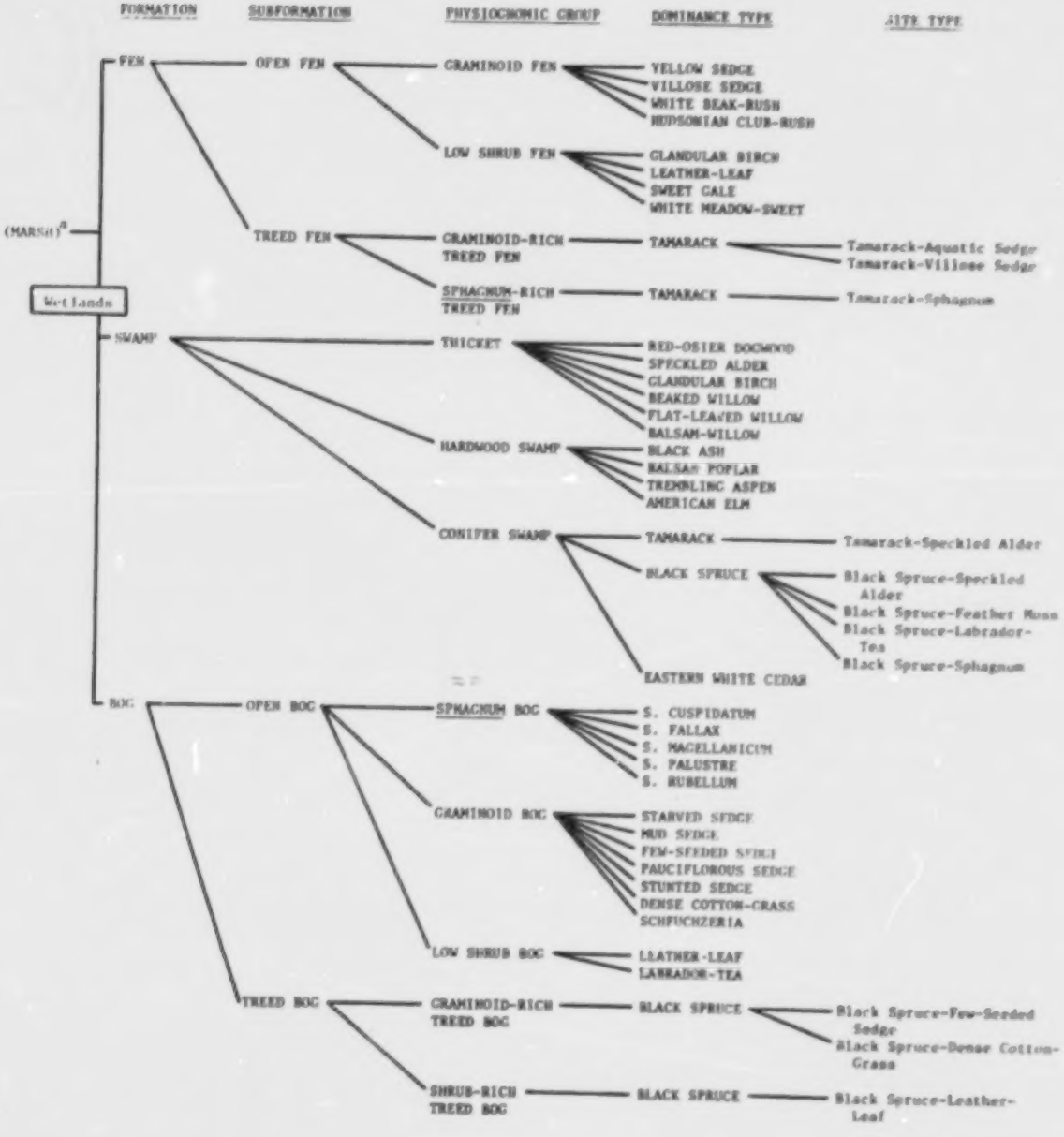
TABLE 1: PEATLAND CLASSIFICATION SCHEME FOR CANADA (Zoltai et al. 1973)[1]

Level 1	Level 2
(SHALLOW OPEN WATER)[2]	
(MARSH)[2]	
BOG	Bowl Bog Collapse Bog Sinkhole Bog Floating Bog Shore Bog Flat Bog Polygonal Peat Plateau Peat Plateau Thermokarst Peat Plateau Bog Plateau Palsa Bog Peat Mound Bog Blanket Bog Raised Bog
FEN	String Fen Seepage Fen Net Fen Floating Fen Shore Fen Draw Fen Horizontal Fen Pond Fen Collapse Fen Palsa Fen Spring Fen Slope Fen
SWAMP	Alluvial Swamp Lakeside Swamp Peat Margin Swamp Catchment Swamp Seepage Swamp

[1] Allowance is made for Levels 3 and 4 modifiers, but no classes are stipulated.

[2] Subdivisions occur, but these are not considered as peatlands.

FIGURE 3: HYDROGEOMORPHICAL CLASSIFICATION OF ONTARIO WETLANDS (after Jeglum et al. 1974)



[a] Marsh is not considered a peatland formation but is a wetland formation.

Peatland modelling requires that vegetational classification schemes accurately reflect physico-chemical data sets. Jeglum et al.'s (1974) classes appear to be in agreement with measurable ecological characteristics of peatlands (Stanek, 1977; Stanek et al., 1977). However, the bulk of the existing vegetational data fails to make the class-site connection according to these established schemes, so that the range in quantitative values for species composition, water and nutrient relations and topographic characteristics common to any one class, requires some refinement, preferably based on the results of provincial peatland inventories.

2.0 HYDROLOGY

By definition wetlands are terrestrial ecosystems with strong hydrological links. Most physico-chemical and biological characteristics can be viewed as direct or indirect measures of water source, amount and renewal rate; vegetational characteristics are good indicators of hydrological gradients - species composition, horizontal and vertical heterogeneity, and primary productivity reflect water flux; soil physico-chemical properties such as pH, nutrient concentrations, oxygen content, and peat accumulation rates are directly related to water source and flow.

Accurate determination of water input and output is essential to understanding ecological interrelationships and developing drainage, mining and reclamation strategies. Water balance is commonly described by a mass balance equation which accounts for all water influxes (I) and effluxes (E) in the system. In this way the storage capacity of the peatland (ΔS) can be calculated;

$$I - E = \Delta S$$

This equation may be modified to reflect the contribution of six major water transfer processes:

$$P + I - D - V - E - \Delta S = 0$$

Where,

- P = precipitation
- I = inflow through groundwater and surface flow
- D = discharge through groundwater, seepage + surface flow
- ΔS = storage capacity of the peatland
- V = vertical seepage to deep subsurface layers
- E = evaporation

These processes are shown schematically in Figure 4. Major assumptions inherent in the scheme are conservation of matter and continuity of pathway transfer. In addition, the water balance equation assumes that all pathways are mutually independent.

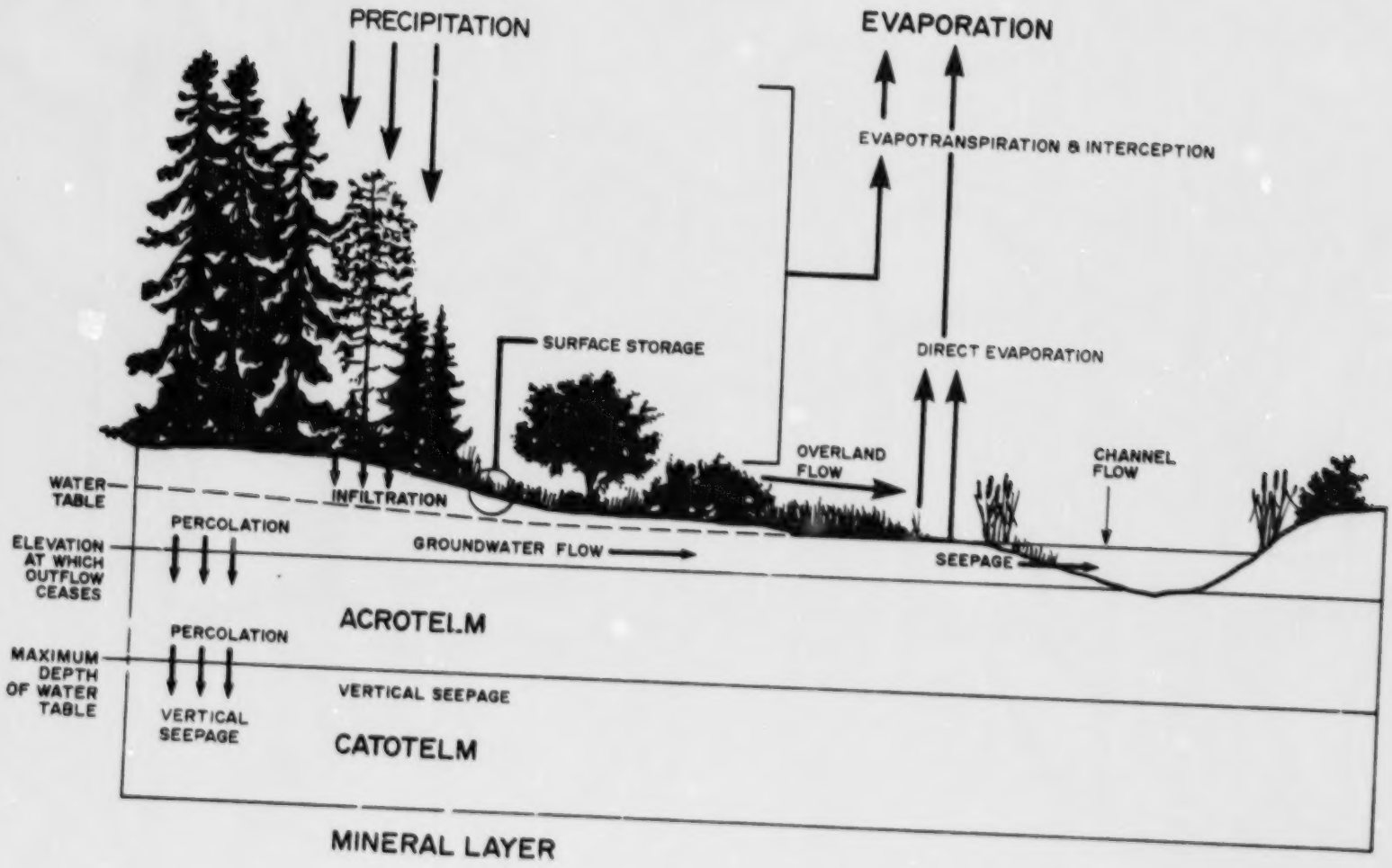


Figure 4 ***Hydrological Cycle of Peatlands***

The relative magnitude of each hydrologic process can be used to differentiate peatland types. Bogs are recharged primarily by precipitation and are largely isolated from the regional groundwater system. Thus, the inflow parameter (I) approaches zero. On the other hand, fens and swamps receive significant groundwater recharge from surrounding mineral soils. The following sections discuss the mechanisms, variability and typical ranges of each of the six major water transfer processes.

2.1 Precipitation

Precipitation is an important control of peatland distribution and type, water table level and runoff. In bogs, precipitation is the major source of water input. Ivanov (1981) has shown that in order for bog formation to occur, net precipitation must exceed net evaporation. In general blanket bogs are found in the wettest locations (i.e., coastal areas), raised bogs occur in relatively wet locations, while swamps and fens predominate in areas were evaporation exceeds precipitation (Ingram, 1983). These observations have been verified by numerous European studies (i.e., Katz, 1971; Taylor, 1976). While no specific data exists for Canadian peatlands, preliminary comparisons of mean annual precipitation with dominant peatland type indicate that this correlation is applicable to Canada.

2.2 Evaporation

Evaporation from vegetation, surface water and peat surface and subsurface layers is the main source of water loss in peatlands (Boelter and Verry, 1977). Total evaporation is the sum of three processes:

Interception - evaporation from plant surfaces which have been wetted by rain, fog, dew, etc.,

Transpiration - evaporative loss of water taken up by plant roots and stored within the plant, and

Direct Evaporation - water loss from plant litter, the peat surface, and subsurface layers.

As might be expected, total evaporation from peatlands is significantly higher than from comparably sized non-peatland catchment areas. The magnitude of evaporative loss is dependent upon the amount of water available for atmospheric uptake, and the rate at which it is taken up. In general, climatic variables control flux rates, and vegetational characteristics determine the amount of available water (Romanov, 1968; Ingram, 1983).

Evaporative rates depend on differences in moisture content between the air and soil. Maximum evaporation occurs when water supply is plentiful and radiant energy flux is high. Radiant energy flux is favoured by relatively low atmospheric relative humidity and warm air temperatures, long periods of solar radiation and low cloud cover. According to Romanov (1968), wind-induced evaporation accounts for less than 10% of total evaporation. His studies in raised Sphagnum bogs indicate that evaporative equilibrium is established at velocities of 1.0 - 1.5 m/sec and further increases have little effect unless temperature inversions are created. Solar radiation is most often the factor limiting evaporation in peatlands. In northern temperate peatlands these trends are clearly discernable. Evaporation isolines show regular decreases with altitude and latitude, and in coastal regions.

Plant transpiration is the major evaporative process. Approximately 90% of annual evaporation occurs during the growing season (Eggelsmann, 1964; Bavina, 1967; Bay, 1968). Diurnal patterns show a maximum at mid-day, and minimum at night, when condensation predominates. Transpiration rates are dependent upon vegetational growth stage, species composition and density, and water table depth. Within a vegetational community, transpiration is relatively constant, however significant differences are observed between species characteristic of bogs and fens. Although precipitation infiltration rates and equilibrium moisture contents are lower, transpiration rates in fens are up to 10% higher than in bogs. Typical values are presented in Table 2.

In raised Sphagnum bogs the hummock- hollow microrelief strongly affects evapotranspiration. The height of capillary rise for most Sphagnum species is limited to 15-30 cm due to the coarse capillary pore size (0.05 mm). The length of the capillary fringe is species-specific; hummocks dominated by S. magellanicum have a longer capillary fringe than those dominated by S. fuscum (Romanov, 1968). Sphagnum also has a low thermal conductivity. Consequently during warm periods, if the water table is close to the surface, transpiration rates are high. However, as the water table recedes and the

TABLE 2: EVAPOTRANSPIRATION IN PEATLANDS

Location and Latitude	Peatland Type	Annual Evapotranspiration (mm) Mean	Range	Author
USSR (Krestunovo)	Fen	594	493-672	Romanov, 1968
USSR	Raised Bog		417-459	Bavina, 1967
Southern Sweden (Komosse)	Peatland Complex		333-429	Johansson, 1974
Northeastern Massachusetts (42°N)	Coastal Raised Bog	1020 (1450)[1]		Hemond, 1980
Northern Minnesota, USA (47°N)	Raised Bog		458-518 (501-578)[1]*	Bay, 1968
Minnesota (47°N)	Raised Bog	533	432-584	Boelter and Verry, 1977
Coastal Germany (53°N)	Raised Bog	499 (742)[1]		Baden and Eggelsmann, 1970
Coastal Southeastern Finland (61°N)	Open Bog/Swamp	430 (500-850)[1]		Seuna, 1981

1 annual precipitation
* based on measurements made between May 1-November 1.

capillary fringe falls below the root zone of the hummock areas, tranpsiration rates drop sharply (Virta, 1966; Romanov, 1968). During mid-summer, evaporation from pools can exceed that from hummocks by 21-33%, depending on water table level (Belotserkovskaya et al., 1969). Similar microrelief effects can be seen over the entire bog. Transpiration rates at the dome are often 20% less than in lagg and pool areas.

The factors controlling evapotranspiration in fens are similar to those in bogs, however the regular inflow of groundwater provides fens with a buffer against extreme dessication. Unlike bogs there is no sharp decline in transpiration with water table depth since higher plant species diversity leads to a deeper more uniform distribution of plant roots.

Direct evaporation from the ground surface and peat layers contributes a maximum of 10% of total evaporation and is effective to soil depths of up to 20 cm depending on radiant energy, soil moisture content and characteristics of the surface peat. Direct evaporation occurs mainly in the evening or night when the temperature of the surface layers exceeds air temperature. Evaporation from lakes and pools within the peatland may contribute significantly to evaporation.

2.3 Inflow

The inflow (I) parameter of the water balance equation represents the total amount of water entering the peatland through groundwater seepage and surface flow. By definition ombrotrophic bogs have an inflow equal to zero, since they receive all of their water input through precipitation. However, in reality few bogs are completely ombrotrophic; the perimeters of most receive runoff from upland mineral soils and large peatlands contain areas of ombrotrophy and minerotrophy. Nonetheless the contribution of inflow to the water balance equation of ombrotrophic peatlands is so small relative to the other parameters that the assumption that inflow (I) approaches zero in such systems is reasonable for the purposes of peatland classification and modelling.

The inflow of surface and groundwaters is highly variable in minerotrophic systems. Functional peatland classifications ranging from transitional bog, poor to rich fen and swamp are included in this group. Inflow rates and volumes are largely determined by:

- o the size of the drainage basin and the location and size of the peatland within it
- o precipitation and hydrological regime
- o peatland topography
- o physical properties of the peat which affect hydraulic conductivity
- o the composition and growth stage of peatland vegetation

Large errors are commonly associated with the measurement of inflow, due to the number of potential sources, their seasonal variability and accuracy of existing equipment (Chebotarev, 1962; Brooks and Predmore, 1978).

2.4 Water Storage

In undisturbed peatlands, water is stored on and in the vegetation, on the ground, in lakes and surface streams, or in topographical depressions. But by far the largest storage compartment is the peat itself.

The high water-holding capacity of peatlands is perhaps their most ecologically distinctive feature. In most bogs and fens the water table remains between 4-30 cm below the surface throughout the year. Even extremely low water tables (i.e. 80 cm) are significantly higher than the average of 150 cm commonly recorded in mineral soils. (Godwin, 1931; Romanov, 1968; Eggelsmann, 1978).

Water storage capacity and transmissability are not uniform throughout the peat profile. Two basic hydrological units are generally recognized (Romanov, 1968; Ivanov, 1981; Ingram, 1983):

1. the <u>acrotelm</u>, or <u>active layer</u>, which includes the aerated surface peat layers, and is delimited by the maxium depth of the water table, and
2. the <u>catotelm</u>, or <u>inactive layer</u>, which includes all peat below the maxium water table depth, and is delimited by the mineral substrate.

In a recent paper based on long-term hydrological studies of Minnesota peatlands, Verry (1984) suggests that the common boundary of these two zones be based on the maximum depth of the water table under <u>nondrought</u> conditions.

Changes in water storage capacity in undisturbed peatlands are generally associated with fluctuations in water table depth within the acrotelm (Novikov, 1964; Hemond, 1980; Ingram, 1983). On the basis of this feature peatlands have traditionally been classified as natural sponges or reservoirs which store water during periods of high flow and slowly release it under drier conditions (i.e. Crawford, 1969). However, numerous studies have shown that the short-term storage capacity of peatlands is largely related to the depth of the water table (Novikov, 1964). While the flat topography and high permeability of the surface peat detains water flow under certain conditions, the temporary storage capacity is generally lower than that of mineral soils or drained peatlands which have lower water tables (Boelter and Verry, 1977; Jansson, 1982). Likewise, there is no quantitative evidence to support the theory of water release during dry periods. In fact, most of the literature indicates that during such periods there is often zero discharge (Section 2.5). Eggelsmann (1972) reports that this layer contains only 3-10% of the total water stored in the peatland, however, from an ecological perspective it is extremely important.

The acrotelm is a dynamic system, characterized by intensive moisture exchange with the atmosphere, vegetation and surrounding catchment area. Large concentrations of aerobic bacteria and fungi constantly modify the physical properties of the peat through decomposition (Ivanov, 1981). The net amount of water input to the system determines the amount of water available for storage. Recharge through precipitation, groundwater and surface flow is offset by evaporative losses.

The characteristics of the surface peat determine the amount of water retained in the acrotelm. Botanical composition, humification and related physical characteristics such as porosity and bulk density exert strong influences on water retention capacity; living or poorly humified Sphagnum, composed of large (> 0.5 mm) pores, yields water readily; Hypnum - sedge peats have smaller pores, which retain water through matric forces (Romanov, 1968; Paivanen, 1973; Ingram, 1983). Other factors which have been found to increase water retention include increasing depth and compaction (Boelter 1969, 1970, 1976). Section 4.0 provides a more detailed discussion of physical properties of peat.

Based on these characteristics, signficant differences in average water table depths are observed between bogs and fens. Sphagnum peats give up water more easily than hypnum sedge peats and hence average water table depths are greater in bogs than fens. Ivanov (1981) reports that typical acrotelm depths in Russian peatlands range from 60-70 cm in ombrotrophic bogs to 5-7 cm in rich fens.

The catotelm is the major water storage unit. It is characterized by moderate to highly humified peats which are permanently waterlogged. Water content is considered to be relatively constant. Much of the water in the catotelm is bound through sorption, or within the cells and capillaries of the decayed organic material. Romanov (1968) found 11-30% of the water in a bog catotelm was bound by surface forces, with the highest percentages recorded in moderately decomposed peat as opposed to undecomposed or highly decomposed material. Kay and Gert (1977) suggest that moderately decomposed peat contains a high percentage of small pores with a minimum of hydrophobic decompositional residues.

2.5 Discharge

Peatland runoff characteristics are directly related to water table depth, hydraulic gradient and the hydraulic conductivity of the peat. When the water table is high, the storage capacity of the peatland is low, and further addition of water is likely to lead to runoff. Water may be discharged through surface flow or seepage. Surface flow includes overland or sheet flow and open channel or track flow. Subsurface discharge generally occurs by lateral seepage through the peat or between strata. Vertical seepage between the acrotelm and catotelm is considered to be negligible. Due to the relative impermeability and low hydraulic conductivity of the deeper more decomposed peat layers, most runoff is from the acrotelm. Velocities of up to 2.5 cm/sec have been recorded in poorly decomposed Sphagnum peats (Romanov, 1968).

Northern temperate peatlands exhibit characteristic seasonal fluctuations in runoff volumes which are related to climatic conditions. These differences are largest in ombrotrophic bogs which receive most of their water input from precipitation. In continental peatlands, up to 2/3 of annual runoff occurs between March and June, when snowmelt and spring rains coupled with high soil moisture and low evapotranspiration raise the water table to levels which are at or above the ground surface (Bay, 1968, 1969; Boelter and Verry, 1977). Under these conditions water storage capacity is effectively zero, and any additional precipitation will result in runoff. During the summer, plant growth and increased solar radiation lead to increased evapotranspiration. Water tables may decline sharply even when rainfall is abundant. For example, Godwin (1931) reported a 3-4 cm diurnal decline in the water table depth of an English fen as a result of evapotranspiration. Consequently, summer is generally characterized by low discharge

volumes. In ombrotrophic bogs which receive abundant solar radiation and little precipitation, runoff may cease altogether (Bay, 1969; Baden and Eggelsmann, 1970; Bavina, 1975). In minerotrophic systems a groundwater baseflow is maintained throughout the summer, although, Vecchioli et al. (1962) note that evapotranspirational losses from minerotrophic peatlands may reduce regional groundwater baseflow volumes by up to 25% during the peak growing season. Few studies report fall discharges, although, autumn flow appears to be associated with precipitation (Bay, 1969; Bavina, 1975; Hemond, 1980). Discharge from raised bogs ceases during the winter months in areas where freeze-up occurs. Descriptions of discharge in minerotrophic systems which freeze are limited but it appears that small baseflows from subsurface layers are maintained throughout the winter (Bavina, 1975).

In northern temperate coastal areas, winters are characterized by numerous freezes and thaws. Peatland discharge in such areas reflects the climatic cycle with peak discharges following thaws (Conway and Millar, 1960; Baden and Eggelsmann, 1970). Eggelsmann and Schuch (1976) report that 79% of annual discharge from a coastal bog system in northern Germany occurred during the winter months. In systems where freeze-up seldom or never occurs, discharge peaks may or may not occur and runoff patterns depend on rainfall distribution (Robertson et al., 1968).

Prolonged heavy rainfall can result in increased discharge from both bogs and fens, even during low discharge seasons. Analyses of storm hydrographs indicate that raised bogs have limited capacity to attenuate storm discharge (Bay, 1969). Peak discharges were observed between 1.0 - 9.0 hours after the storm event. Time differences were attributed to differences in water table depth, hydraulic gradient and conductivity of the peat material. Minimum lag times and maxium runoff peaks were recorded when water table levels were high prior to the storm event. Recession curves for raised bogs exhibit a steep initial slope, representing runoff from the upper layers of the acrotelm, followed by a more gradual decline as the water table recedes through the more decomposed peat to pre-storm levels (Dingman, 1966; Bay, 1969). During the growing season the recession curve may exhibit sharp diurnal fluctuations due to evapotranspiration. Fen hydrographs show a delayed response to storm events. Since minerotrophic peatlands act as surface discharge points for regional groundwater systems, their runoff characteristics reflect hydrogeologic changes over the entire catchment area.

It is interesting to note that while bogs and fens exhibit basic differences in seasonal discharge behaviour, maximum discharge rates in areas of similar climate appear to be independent of peatland type. Boelter and Verry (1977) suggest that streamflow rates are determined by watershed size and percentage of peatland, amount and intensity of precipitation (including the water content of the snowpack and rate of snowmelt), and infiltration characteristics of the basin soil.

3.0 PEATLAND VEGETATION

Vegetational characteristics form a major component of any ecological study. Composition, diversity, succession and productivity are sensitive indicators of key abiotic factors. In peatlands, vegetation is especially important since it is the precursor of peat and is, therefore, either directly or indirectly implicated in all major physico-chemical processes. The following section describes critical aspects of peatland vegetation ecology as they relate to ecosystem modelling.

3.1 Peatland Succession and Evolution

3.1.1 Successional Scenarios

Analyses of peat cores typically reveal profiles consisting of distinct layers of differing botanical origin and/or decompositional state. These strata depict successional trends which reflect vegetative response to changes in key controlling variables, such as climate, topography, hydrology or anthropogenic effects. Since the stratified nature of the peat has a strong influence on many physical and chemical properties of the peatland, understanding the successional sequences which led to peat formation is of vital interest.

Characteristic peatland successional sequences for North America are presented in Tables 3 and 4, and Figure 5. The most common sequence is of open water to wetland, to upland. However, in some cases, particularly in complex peatlands, succession appears to follow anomalous patterns. In still other instances, externally induced changes may alter peatland development. As a result, many (often conflicting) theories of wetland succession have been developed.

Several of the more widely accepted theories are summarized below. These are largely extracted from Tallis' (1983) summary of changes in wetland communities.

Terrestrialization Scenario of Weber (1908) and Clements (1916)

This is the classical development of peatlands from basin waterbodies which become infilled and provide habitat for aquatic and finally terrestrial plants:

TABLE 3: GENERALIZED PEATLAND SUCCESSIONAL SCHEME FOR BOREAL NORTH AMERICA* (Erskine, 1977)

Successional Stage	Time Scale
Open water with submerged aquatic vegetation	Time scale varies greatly with site conditions, including topography, soils, water temperatures
Water areas with emergent vegetation well out from shore	
Wet areas with some standing water and shrubby as well as herbaceous vegetation; the first small tamaracks may appear here	Probably at least several hundred years from open water **
Damp areas (water shows only when surface mat is depressed) with shrub and moss hummocks and well-spaced small trees - tamarack or black spruce	Perhaps 10 to 100 years from previous stage, depending on precipitation cycles and drainage**
Damp areas with low forest of tamarack or black spruce	Perhaps 20 to 50 years from previous stage, unless halted by rising water table
Dense, medium-aged forest of black spruces, with some balsam fir regeneration	Perhaps 25 to 75 years from previous stage
Mature black spruce forest with some younger balsam fir of varying ages	Perhaps 25 to 75 years from previous stage

* These stages are most often recognized as concentric zones around the edges of a depression or strips along the edges of a blackwater stream; except for very small depressions, this sequence need not be viewed as inevitable.

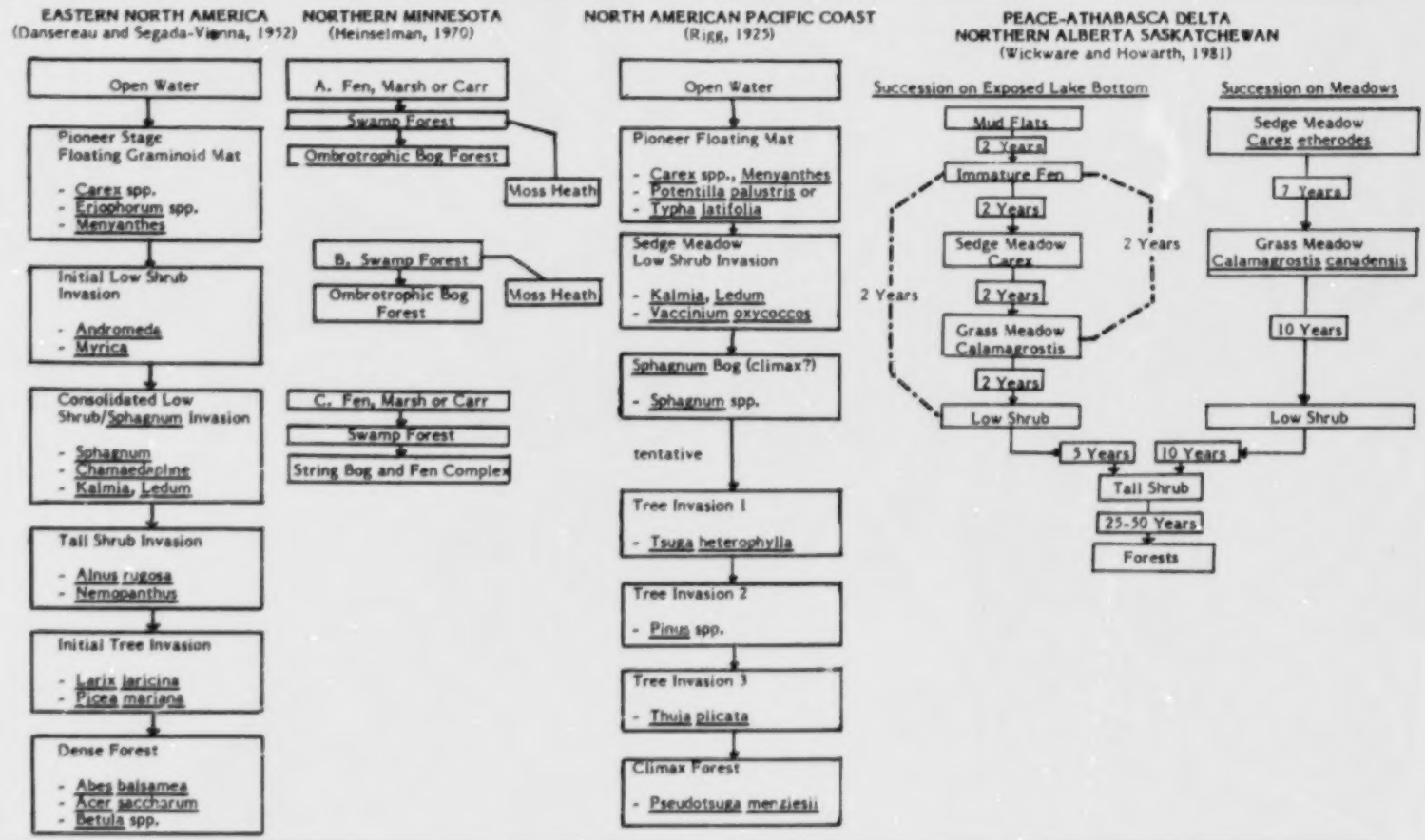
** The time scales given are little more than educated guesses.

TABLE 4: EVOLUTION OF LAKE AGASSIZ (MINNESOTA) PEATLANDS

Time Scale (Year B.P.) (approximate)	ORIGINAL POST-LAKE AGASSIZ PHYSIOGRAPHY: BASINS	GENTLY-SLOPING	PLAINS	UPLAND BEACHES, RIDGES	PEAT FORMING EVENTS	CLIMATIC EVENTS	SEDIMENT/SUBSTRATE EVENTS	HYDROLOGIC EVENTS	WATER CHEMISTRY EVENTS	TOPOGRAPHIC EVENTS	VEGETATION EVENTS	Details
12,000	x	x	x				x	x		x		Lake Agassiz covers area; primarily inorganic sedimentation
11,740	x	x	x				x	x		x		Lake Agassiz recedes from Herman Beach, with inorganic sedimentation/deposition
11,600-10,000		x	x								x	Spruce forest or spruce parkland present
11,120-10,310	x						x	x				Organic gyttja formation
10,000-8,000		x									x	Elm, white spruce, fir, cedar, aspen, balsam poplar, ash probably dominate
10,000-8,000			x								x	Jack pine, red pine probably dominate
8,000	x	x	x	x	x							Postglacial warm-dry interval begins
(8,000)-			x								x	Oak savannah or local prairies apparently dominate
(8,000)-		x		x			x	x		x	x	Fens, marshes, carr overspread lower ground and paludification begins; sedge peats cover nearly half of area; water table rises 0.9-2.4 m; early marsh lakes overgrown
5,000		x	x	x	x				x		x	Increased precipitation; white pine and other species invade uplands; swamp forests of Picea, Larix, Thuja begin to invade fens and carrs and expand laterally onto uplands, building forest peats. Swamp forests also include sedges, grasses, mosses, herbs, shrubs of Betula, Alnus, Salix. Groundwater minerotrophic
5,000-3,000	x			x		x	x			x	x	Remaining water basin rises during period of paludification; lake drains by percolation through peats and surface runoff; aquatic sedimentation continues, but no development of emergent vegetation; forest peats surround lake
3,100	x	x	x			x	x			x		Water table divide/stream capture as peatland topographic elevation increases; invasion of Sphagnum over wide areas; diversification of peatland types and of water nutrient status; first ombrotrophic vegetation types
(3,100)-	x	x	x	x	x					x		Changed to resemble today's pattern; excess precipitation over evapotranspiration; water divide induces peatland erosion; surface levels out somewhat; increased rate of Sphagnum peat accumulation in raised bog areas
2,700	x										x	Sphagnum invasion of remaining water basins
Present	x	x	x			x	x			x	x	Most basins not identifiable, but one has remained and although smaller, has not succeeded. This one at surface has risen 3.6 m. Raised bogs support ombrotrophic Sphagnum-black spruce communities on crests; nearly treeless Sphagnum-heath on slopes; stunted Larix-heath-sedge on drains. Fen, swamp and bog communities show considerable increase in diversity of types, compared to earlier periods.

Source: Heinselman 1970

FIGURE 5: CHARACTERISTIC PEATLAND SUCCESSIONAL SEQUENCES



Lake mud ⟶ Peat mud (limnetic) ⟶ Phragmites peat ⟶ Alnus wood peat ⟶ Pinus-Betula wood peat ⟶ Scheuchzeria or Carex-Sphagnum peat ⟶ Sphagnum peat.

Basin infilling is caused by death of aquatic and wetland plants plus inorganic sedimentation. During infilling, a stage occurs where the surface vegetation is only seasonally waterlogged. Thus, the surface layers are not influenced by laterally flowing nutrient-rich water, and ombrotrophic, oxygen deficient conditions occur which favour vertical accumulation of peat. A convex water table is maintained by a combination of excess precipitation over evapotranspiration and capillary water movement.

Anomalous intervening or spatially interspersed sequences may be influenced by the effect of a certain community on the permeability of the surface. Other anomalous sequences can be explained in terms of allogenic climatic changes, or other disturbances (see Items 2 and 3 below).

Recurrence Scenario of Von Post and Sernander (1910) and Osvald (1923)

This scenario explains sharp changes from well-humified to poorly humified peat in ombrotrophic peatlands, through autogenic changes. It hypothesizes that spatial variation in peat accumulation leads to the formation of open water pools, which are slowly encroached upon. The patches are then subject to greater accumulation and vertical growth.

This theory was extended by Osvald (1923) in his hummock/hollow complex scenario; rapid upward development occurs during growth of one vegetation association, which results in increasing hummock surface dryness and growth of communities which do not accumulate peat so rapidly. Intervening hollows continue to expand vertically, bringing with them a rise in water table, thus waterlogging the degenerating hummocks and converting them into hollows.

Water Supply Model Scenario of Peatland Development of Kulczynski (1949)

Wetlands develop according to topography and hydrology. Topographic complexities are resolved into discrete catchment areas of sloping ground which channel water to rivers, and intervening flat areas. Peatlands develop where flow rate is slow enough to prevent

peat erosion. The water table is convex, periodically saturating surface layers through small vertical oscillations in level. Lateral flow gradually concentrates into channels. Vegetation communities develop in response to flow rate and ionic composition of precipitation and groundwater. If long-term changes in water and ion supply occur, vegetation communities will change.

Plants may bring about changes in water level and movement by accumulation of peat which displaces or diverts water. Externally-induced changes caused by climate, damming or drainage can also affect hydrodynamics.

Under conditions of rapid water movement, silt is deposited around the bases of reed-swamp plants and decomposition is rapid due to the high oxygen content of flowing water. Peat builds up slowly and is dense. Although initial flow is over the surface of this peat, it gradually becomes channelled; and areas between the channels are only occasionally affected by flowing water. Here, a slow progression toward ombrotrophic conditions occurs. In areas with low water flow, peat accumulates rapidly in the deoxygenated water, and being of low density, forms a floating mat. This, in turn, impedes water flow (peat dam). The peat surface continues to build upward, drawing with it a convex water table held by capillarity. Ombrotrophic conditions are established in this "raised bog". Floating mats eventually become grounded by continuous peat accumulation.

Non-Traditional Successional Scenarios

Nontraditional views of peatland succession centre around situations where the peatland is not a simple isolated basin, but a complex with groundwater and nutrient variations, topographic complexities and a history of alterations in peatland types that do not follow the traditional successional sequences.

Anomalous peat accumulation patterns can result from self-induced or external influences. As a peatland continues to expand vertically, a point may be reached, under static climatic conditions, where its own topography prevents further growth, due to one or more of:

- enhanced gravitational flow (hydraulic head),
- erosion by surface water, and
- desiccation and increased decomposition rate.

At any stage, climatic change can lead to either resumption of the vertical peat accumulation, i.e., through increased precipitation or reduced evaporation caused by cool wet conditions, or slowdown of development (by warm and/or dry climate). Various dates for onset and discontinuance of wet/cool and dry/warm conditions in the world's peat-forming areas are given in the literature (Heinselman, 1970; Tallis, 1983). In the same vein, the local climate at any one point in time varies according to continentality, air mass influence, etc., and vertical peatland development has been successfully correlated with these conditions (e.g., Granlund, 1932, cited by Tallis, 1983, p. 316).

These generalizations must be tempered by considering the increased potential of peat surface erosion if wet conditions pass a critical level. River erosion can lead to cessation of growth in valley and upland peatlands. Tectonic events, including uplift, post-glacial (isostatic) rebound, subsidence by groundwater solution of certain bedrock types and changes in sea level, may also be factors.

In his detailed study of northern Minnesota peatlands, Heinselman (1970) notes that the evolution of complex peatlands must account for the following observed trends and factors:

- original climatic parameters of temperature and precipitation, and evapotranspiration ratios, including vegetational response to subsequent alterations; also includes nutrient/chemical status of precipitation;
- original topographic variables including watershed catchment area, average slopes, distribution of basins, gradual slopes and elevated areas;
- substrate type, both in the original formative area and its surroundings, and in the surroundings as altered by long-term tectonic, erosional, vegetational and soil-forming processes;
- the potential for and distributional aspects of paludification, whereby a peatland expands vertically and horizontally as a result of autogenic accumulation of peat; and

- induced changes in groundwater levels, changes in nutrient status, flow rates and flow directions in response to climatic change, paludification and surrounding topography.

Thus, in order to account for successional changes, virtually all aspects characteristic of peatlands (and surrounding areas) come into play.

3.1.2 Rate of Succession

Successional encroachment on open water can be rapid in some cases; in a 24-year period, a horizontal advance of 46 m was recorded at Mud Lake Bog, Michigan (Gates, 1942); Jewell and Brown (1929) described total encroachment on Cecil Bog, Michigan over an area of 92 x 18 m in only three years. Other peatlands apparently remain unchanged for long periods; Buell et al. (1968) found no change in the position of a sedge mat margin at Cedar Creek Bog, Minnesota, between 1934 and 1967, although succession to the tree invasion stage reduced the mat dimension from 23 m to 3 m. A reverse trend of encroachment of open water on sedge mat has also been reported, in response to periods of increased precipitation (Floating Bog, Minnesota) (Isaak et al. 1959). Succession on deltaic deposits, such as the Peace-Athabasca delta, may be very rapid (see Figure 5) (Wickware and Howarth, 1981).

Longer term successional periods are generally the rule in northern latitudes. However, it is difficult to infer values other than by combining data on peat age (carbon-14 dating) and pollen analysis. Rates of change over long periods are, however, contingent on many local factors which can rarely be generalized into an "average" value, because of variable accumulation rates, hydrological factors, etc.

Under conditions of rapid peat accumulation, successional changes can also occur rapidly. Accumulation is greatest under ombrotrophic conditions. Sphagnum bogs might therefore be expected to change more rapidly than some other seral stages. However, consideration must also be given to the ecological conditions required by a potentially successive community. Because of the tendency for Sphagnum bogs to draw the water table upwards, the community is maintained until a maximum topographic limit is reached.

3.2 Factors Influencing Peat Accumulation

Peatlands of temperate, boreal, subarctic and arctic regions have several biogeochemical features in common, but measures of their biomass and productivity (NPP) show considerable overlap with nonpeatland classes. These are often a result of category definition. For example, arctic peatlands have high biomass and productivity levels compared to other arctic ecosystems (Table 5). However, the definition of peatlands as inclusive of certain types of extensive, moderately to highly productive swamp and marsh (inherent in the Table 5 classification), overshadows the pervasively low biomass and productivity levels of bogs and many fens. Soil-vegetation formations provide a better perspective of differences between peatland and non-peatland areas (Table 6).

Bog biomass varies relatively little with latitude (2500 to 4000 g/m^2), but productivity increases dramatically in warm climates (Table 6). Fens show a parallel, but more marked increase in biomass and productivity in the warmer zones, and swamps probably also do, but classification overlap of fen with nonpeatland marsh, and of swamp with mesic forest is highly likely.

It is apparent at these levels of classification, that biomass and productivity data do not, of themselves, distinguish peatlands. Other parameters, such as litter accumulation, may be more useful in doing so (Table 7).

3.2.1 Biomass

Biomass is the total standing mass of organic matter associated with living flora and/or fauna. Definition of the term varies somewhat, but never includes litter, excreta or exudates which have become disassociated with the living biota. Forest biomass has been studied extensively, with numerous data and equations listed in the literature (e.g., Stanek and State, 1978). Many of these refer to upland forest biomass, but some include treed peatlands, or could be inferred to do so. Biomass figures for open bogs and fens are also available, but not extensively so, for Canadian peatlands. Clearly, when densely forested swamps are included, along with poor bogs, the range in biomass values (generally given as oven dry mass per unit surface area) is very large. Selected biomass data for Canadian and other peatlands are given in Table 8.

TABLE 5: BIOGEOCHEMICAL COMPARISON OF PEATLAND AND NON-PEATLAND ECOSYSTEMS (NPP-Net Primary Productivity)

Type[1]	Thermal Belt or Ecosystem Complex	Bioclimatic Region	Biomass Range (g/m^2)	Percent of Global Thermal Belt Biomass	Annual NPP (g/m^2)	Percent of Global Thermal Belt NPP
Non-peatland	Polar Belt	humid and subhumid	500-2,800	96.5	70-250	96.7
Peatland			1,000-2,500	3.5	170-220	3.3
Non-peatland	Boreal Belt	humid and semihumid	3,500-37,000	75.6	400-1,200	76.4
Peatland			3,500-26,000	24.4	350-700	23.6
Non-peatland	Subboreal Belt	humid	3,500-40,000	95.4	1,200-1,300	92.4
Peatland			4,000-30,000	4.6	1,200-2,500	7.6
Non-peatland	Subtropical Belt	humid	3,000-45,000	88.4	1,300-2,000	59.1
Peatland			25,000-40,000	11.6	2,200-13,000	40.9

[1]Broadly interpreted from vegetation description.

Adapted from Rodin et al. (1975)

TABLE 6: BIOGEOCHEMICAL CHARACTERISTICS OF PEATLAND AND NON-PEATLAND ECOSYSTEM TYPES (NPP = Net Primary Productivity)

Thermal Belt / Bioclimatic Region / Vegetation - Soil Type	INTERPRETED PEATLAND/NON-PEATLAND CLASS (Likelihood of Class Overlap with Interpreted Class)[1]							
	BOG		FEN		SWAMP		NON-PEATLAND	
	Biomass (g/m^2)	Annual NPP (g/m^2)	Biomass (g/m^2)	Annual NPP (g/m^2)	Biomass (g/m^2)	Annual NPP (g/m^2)	Biomass (g/m^2)	Annual NPP (g/m^2)
A. POLAR BELT								
1. Humid and Subhumid								
1.1 Polar bogs on bog permafrost soils	2,500	220	(M)		(U)		(L)	
1.2 Floodplain formation	(U)		1,000	170	(M)		(M)	
1.3 Polar deserts	(U)		(U)		(U)		500	100
1.4 Tundra on gley soils	(U)		(U)		(U)		2,800	250
B. BOREAL BELT								
1. Humid and Semihumid								
1.1 Middle taiga forest on podzolic soils	(U)		(U)		26,000	700	(H)	
1.2 Southern taiga and mixed broadleaf/needle forest on taiga bog soils with bogs	(U)		(U)		8,000	400	(L)	
1.3 Bogs	3,500	350	(M)		(U)		(U)	
1.4 Floodplain formations	(U)		6,000	600	(M)		(M)	
1.5 Mountain meadows on gray forest soils	(U)		(U)		(U)		3,500	1,200
1.6 Broadleaf forest on gray forest soils	(U)		(U)		(U)		37,000	800
C. SUBBOREAL BELT								
1. Humid								
1.1 Broadleaf forests, swampy, with small bog areas	(L)		(L)		30,000	1,300	(H)	
1.2 Bogs	4,000	2,500	(M)		(U)		(U)	
1.3 Flooplain formations	(U)		9,000	1,200	(H)		(M)	
1.4 Herbaceous prairie on meadow brunizems	(U)		(L)		(U)		3,500	1,500
1.5 Broadleaf forests on brown forest soils	(U)		(U)		(L)		40,000	1,300

[1] Likelihood of class overlap (U) unlikely; (L) low likelihood; (M) moderate likelihood; (H) high likelihood

Source: Rodin et al. (1975)

TABLE 7: INTENSITY OF MINERAL CYCLING IN SOME WOODLAND ECOSYSTEMS

	Soil Litter (L) (tonnes/hectare)	$\frac{L}{\text{Annual Litter}}$ Autumn	Cycle
Sphagnum forest	80	50	stagnant
Taiga	30 to 45	10 to 17	very retarded
Deciduous forest	a	3 to 4	retarded
Steppe	4 to 6	1 to 1.5	intensive
Subtropical forest	10	0.7	intensive
Savanna	1 to 2	0.2	very intensive
Equatorial forest	-	0.1	very intensive

[a] - Changes with time of the year and type of humus.

After Rodin and Bazilevich (1967)

TABLE 8: BIOMASS IN PEATLANDS

Site	Dominant Vegetation or Type	Interpreted Type	Biomass (g/m^2) Shoots	Below-Ground	Other	Reference
A. CANADA						
1. Devon Is., NWT	Sedge meadow	Fen	60-90			Muc 1973
2. Northern Manitoba	Treed Bog	Treed bog				Sims & Stewart 1981
	Trees		228			
	Dwarf shrubs		395			
	Herbs		35			
	Graminoids		10			
	Ground lichens		78			
	Bryophytes		48			
	Total		794			
	Disturbed Treed Bog (7 yr.)					
	Trees		0			
	Dwarf shrubs		175			
	Herbs		20			
	Graminoids		14			
	Ground lichens		negligible			
	Bryophytes		2			
	Total		210			
B. OTHER, NORTHERN NORTH AMERICA						
1. Point Barrow, Alaska	Wet sedge meadow	fen	100			Tieszen 1972a
C. OTHER, TEMPERATE TO POLAR						
1. Hardangervidd, Norway	Lichen heath		30-60			Wielgolaski 1972
	Dry and wet meadow	(fen)	90-140			
2. Taimyr, USSR	Moss - Dryas - sedge tundra	(fen)	100			Shamurin et al. 1972
3. Abisko, Sweden	Bog	bog	110			Rosswall 1972
4. Western Taimyr, USSR	Dwarf shrub/sedge/moss/lichen tundra	bog or fen	188			Pospelova 1972
5. Taimyr, USSR	Polygonal bog	bog	190			Shamurin et al. 1972
6. Salekhard USSR	Moss-shrub-hummock	bog	204			Gorchakovsky and Andreyashkina 1972
7. Glenamoy, Ireland	Open bog	bog	214			Moore (cited by Wielgolaski 1975
8. Western Taimyr, USSR	Flat palsa bog	bog	513			Pospelova 1972
9. Hardange vidd, Norway	Willow thicket	swamp	800			Kjelvik & Karenlampi (cited by Wielgolaski 1975)
10. Eastern Europe, USSR	Shrub tundra	(swamp or bog or fen)	817			Alexandrova 1970
11. Moor House, U.K.	Blanket bog	bog	846			Forrest 1971
	Blanket bog: Calluneto-Eriophoretum (summer)	bog	1,564			

Peatland biomass can be subdivided into constituent parts on the basis of one or more of the following:

- species
- ecological function (e.g., autotrophs, heterotrophs, consumers)
- age classes of flora or fauna
- classes of species (e.g., trees, dwarf shrubs, herbs, graminoids, lichens, bryophytes, herbivores, insectivores, carnivores, etc.)
- peatland physiognomic or vegetation class
- frequency of occurrence (e.g., based on ordination techniques, indicator species, rare and endangered species, seasonally relevant species, etc.)
- parts of species (stem, roots, leaves, reproductive structures, photosynthetic parts, woody parts, etc.).

3.2.2 Net Primary Productivity

Biomass and net primary productivity (NPP) are closely related. Primary productivity is the net rate of storage of organic matter in plant tissues. Gross primary productivity includes respiratory organic matter and is not reported in most studies. NPP includes the mass of litter formed during the measurement period. In peatlands, litter is, of course, the dead biological matter which, in time, accumulates to form peat.

NPP values are important in peatland modelling because they can be used to balance macro- and micro-element fluxes and to aid mass balance computations involving meteorological input, evaporation, runoff, leaching/seepage and incorporation in living tissues. For example, estimates of rates of vegetative uptake of trace metals and nutrients can be derived via tissue analysis and application of the NPP data.

Although insufficient information is available to rank Canada's peatlands according to NPP, some typical ranges of values are available (Table 9). Bog, fen and swamp vegetation types are poorly differentiated in these results, but it appears that swamps are most productive, with a general range of 1500-2000 g/m^2/year (OM), while fens and bogs are in the 300 to 1000 g/m^2/year range (Bradbury and Grace, 1983). Peatland productivity levels in Canada appear comparable to those reported in temperate to polar peatlands elsewhere.

TABLE 9: NET PRIMARY PRODUCTION IN PEATLANDS

Site	Dominant Vegetation or Type	Interpreted Peatland Type	Annual Productivity (g/m^2) Shoots	Below Ground	Reference
A. CANADA					
Quebec	Carex spp.		820	205	Auclair et al. 1976a
Southern Quebec	Scirpus spp./Equisetum fluviatile	marsh	914	-	Auclair et al. 1976b
Manitoba	Ombiotrophic peat bog	bog			Reader & Stewart 1971
	Non-vascular species		55.4	-	
	Vascular species		316.4	1,461.1	
	Total		371.8		
Southern Manitoba	Bog marsh/lagg	fen			Reader & Stewart 1972
	Chamaedaphne calyculata		227		
	Carex rostrata		116		
	Calamogrostis canadensis		48		
	Salix bebbiana		219		
	S. serissima		11		
	Aulacomnium palustre		36		
	Hypnum pratense		31		
	Others		338		
	Total		1,026	513	
	Salix spp./Carex spp./bryophytes	fen or swamp	1,118	513	
	Conifers/bryophytes	swamp or bog	523	187	
	Ericaceous shrubs/bryophytes	bog	482	1,461	
	Ericaceous shrubs/bryophytes/ conifers	bog or swamp	399	594	
	Pleurozium schreberi		108	-	Busby et al. 1978
	Polytrichum juniperinum		35	-	
Central Alberta	Homalothecium nitens		190	-	
	Typha latifolia	marsh	322	-	Van der Valk & Bliss 1971
	Eleocharis palustris		341-447	-	
	Equisetum fluviatile	marsh	491-707	-	
	Alisma plantago-aquatica		444	-	
Western Alberta	Carex aquatilis	fen or marsh	550	-	Gorham & Somers 1973
	Carex rostrata		740	-	
Devon Is., NWT	Various spp.		10-293	-	Pakarinen & Vitt 1973
	Sedge meadow	fen	42-115	70-191	Muc 1973
Dempster, Yukon	Cottongrass tundra	fen			Wein & Bliss 1974
	Eriophorum vaginatum		27		
	Ledum palustre		4		
	Vaccinium vitis-idaea		2		
	Carex spp.		1		
	Betula nana		4		
	Rubus chamaemorus		3		
	Andromeda polifolia		.2		
	Lichens		1		
	Mosses		127		
	Total		169		
B. OTHER, NORTHERN NORTH AMERICA					
Michigan	Alnus rugosa/Fraxinus niga	swamp	570-640		Parker & Schneider 1975
New York	Carex lacustris	marsh or fen	1,580		Bernard & MacDonald 1974
	Alder shrub community	swamp	950	-	Tilton & Bernard 1975
Wisconsin	Carex lacustris	marsh or fen	1,034	147	Klopatek & Stearns 1978
	Typha latifolia	marsh	1,643	1,550	
	Phalaris arundinacea	marsh	1,353	675	
	Scirpus fluviatilis	marsh	1,116	417	
Minnesota	Typha hybrid	marsh	1,440-1,680	-	Bray et al. 1959
	Various deciduous trees/shrubs/herbs	swamp	707	-	Reiners 1972
	Thuja occidentalis/Betula papyrifera	swamp	1,032	-	Reiners 1972
	Sphagnum	bog (perched)	380		Griegal 1984, pers. comm.
		bog (raised)	320		
Princeton, Minnesota	Sedge wetland	fen or marsh			Bernard 1974
	Carex rostrata		738	180	
	Equisetum fluviatile		42	17	
	Sagittaria latifolia				
	Total		780	197	

TABLE 9: NET PRIMARY PRODUCTION IN PEATLANDS (cont'd)

Site	Dominant Vegetation or Type	Interpreted Peatland Type	Annual Productivity (g/m^2) Shoots	Below Ground	Reference
New Jersey	Typha latifolia	marsh	1,904	-	Jervis 1969
Oregon	Typha latifolia	marsh	418	-	McNaughton 1966
	Typha latifolia	marsh	330	-	
North Dakota	Typha latifolia	marsh	404	-	
Wyoming	Alpine grass/sedge meadow	fen	112	-	Bliss 1962
New Hampshire	Alpine heath shrubland	(fen)	283	-	Bliss 1966
Shelburne Pond W. Bog, Vermont	Leatherleaf-lowshrub peatland	bog	304	-	Osheyack 1980
	Speckled alder/Red maple tall shrub peatland	swamp	294	-	
	Carex lasiocarpa emergent peatland	fen	220	-	
	Typha emergent peatland	marsh	1,982	-	
Alaska	Caltha leptosepala	fen	108	-	Webber 1972
	Deschampsia flexuosa	fen	156	-	
	Salix planifolia	fen, bog or swamp	459	-	
	Sedges/bryophytes	bog or fen	90	-	Anderson 1972
	Sedge meadow	fen	156	-	Brown & West 1970
	Sedge meadow	fen	102	-	Dennis & Tieszen 1972
	Sedge meadow	fen	73	-	Haag 1974
	Wet tundra meadow	fen	101	-	
Eagle Creek, Alaska	Cottongrass tundra	fen			Wein & Bliss 1974
	Eriophorum vaginatum		28		
	Ledum palustre		9		
	Vaccinium vitis-idaea		12		
	Carex spp.		10		
	Vaccinium uliginosum		9		
	Empetrum nigrum		1		
	Betula nana		2		
	Rubus chamaemorus		3		
	Andromeda polifolia		1		
	Lichens		3		
	Mosses		32		
	Total		110		
Barrow, Alaska	Wet meadow	fen			Tieszen 1972a
	Carex aquatilis		25		
	Dupontia fischeri		21		
	Eriophorum angustifolium		29		
	Calamagrostis holmii		3		
	Eriophorum scheuchzeri		10		
	Poa arctica		5		
	Other		8		
	Total		101		
Houghton Lake, Michigan	Leatherleaf-bog birch	fen			Richardson et al. 1976
	Chamaedaphne calyculata		187		
	Betula pumila		151		
	Herbs		3		
	Total		341	100	
Thoreau's Bog, Massachusetts	Sphagnum bog	bog	460	-	Hemond 1980

NPP is influenced by a number of environmental variables. Reader (1982) found several correlations between shoot productivity in three bog species, and seven environmental variables, which accounted for between 95 and 99% of the variability in productivity. These and other potential variables are discussed briefly below.

1. **Latitude:** Northern sites tended to have lower productivities, but altitudinal differences had considerable bearing on this as well. Lower, more northerly sites could be more productive than higher sites even 200 km to the south. Latitude also reflects climatic and insolational variables.

2. **Genetic Variables:** A plant species which grows in widely separated areas may have genetically governed characteristics which influence productivity. This variable has been infrequently investigated in peatland plants.

3. **Heat Sum:** The number of degree-days indirectly reflects the level of insolation reaching the plant's photosynthetic apparatus and also the metabolic rate of many plant biosynthetic pathways. Reader (1982) found a strong correlation with productivity.

4. **Evaporation:** A poor direct correlation with productivity was found by Reader (1982), although increased evaporation leads to cooler temperatures, less efficient use of radiant energy and therefore lower productivity (Bradbury and Grace, 1983).

5. **Water-Table Depth:** Productivity was highly correlated (Reader 1982). Sites with water near the surface tended to be more highly productive. However, it is not clear if this variable is itself independent of water nutrient status. Bradbury and Grace (1983) discuss the topic of water stress (lack of available water) in wetland plants. It appears that this is not an uncommon phenomenon and may account for reduced productivity. Griegel (1984, pers. comm.), working in Minnesota, observes that Sphagnum productivity on hummocks which periodically dry out is less than in hollows.

6. **Water Nutrient Status:** Reader (1982) did not examine this factor directly, although it has received considerable attention elsewhere and has been the basis

for some peatland classifications (Section 6.0), as well as the theorized basis for peatland evolutionary scenarios. Nutrients such as N, P and K are of considerable importance, but other elements are also implicated (e.g., Ca, Mg and some trace elements).

7. **Substrate Aeration:** This variable, may be indirectly correlated with productivity on the basis that oxygenated soils promote greater rates of microbial activity, root development and biochemical processes which in turn make some nutrients more readily available.

8. **Precipitation:** Reader (1982) found a poor correlation with productivity.

9. **pH:** Reader (1982) found a poor correlation with productivity.

10. **Conductivity:** Reader (1982) found a strong correlation with productivity. This again may reflect water nutrient status.

11. **Total Hardness:** Reader (1982) found a significant correlation with productivity at most but not all sites.

12. **Irradiation:** Theoretical and experimental estimates of productivity indicate a direct correlation between photosynthetic rate and solar energy capture. The relationship appears to be linear at low light intensities and progressively less efficient at higher ones (Tanaka et al., 1966; Dykyjova et al., 1970; Monteith, 1972). Plant canopy architecture (shading) and microtopographic variations in incoming radiation affect light intensity.

13. **Length of Growing Season:** A direct correlation with productivity is apparent in most vegetation types.

14. **Species:** A range in potential productivities exists for plant species, and a factor of two or more separates the least and most productive species (Small, 1972; Grace and Marks, 1978). Sphagna appear to be about half as productive as some woody bog species (Bradbury and Grace, 1983). Variables such as type of carbon assimilation pathways (of which several different methods exist) (Mooney, 1972), leaf area and plant architecture are implicated.

15. **CO_2 Supply:** The active photosynthesis occurring over a surface area is responsible for reducing atmospheric CO_2 concentration. Depending on topographic, microtopographic and other factors which influence CO_2 turbulent transfer, productivity can respond accordingly in different peatland settings (Bradbury and Grace, 1983).

3.2.3 Accumulation/Decomposition

To model the hydrogeochemical dynamics of peatlands, data on productivity must be augmented with data on litter production, decomposition (decay) and accumulation rates. In disturbed peatlands productivity and accumulation may be reduced or curtailed while decomposition processes continue, though generally with attendant changes in rates.

As already indicated, litter production rates are incorporated in values of net primary productivity. However, NPP must be subdivided into its litter production, accumulation rate and incremental growth constituents to model some important peatland processes. Litter production rate is normally equal to decomposition plus accumulation rates (assuming no export from the ecosystem).

The litter produced in almost any natural ecosystem undergoes oxidation reactions, export and transformations brought about by heterotrophic bacteria. In many types of ecosystems the litter production rate reaches a steady state level, as does NPP. Furthermore, the litter decomposition rate tends to equal the litter production rate so that no net accumulation occurs (Ovington, 1959; Grier and Cole, 1972; Harris et al., 1975; Foster and Morrison, 1976). Peatlands, however, form under conditions which favour accumulation; i.e., a comparatively waterlogged, anoxic, nutrient poor, acidic environment. Minerotrophic swamp and fen ecosystems tend to permit higher rates of chemical and microbial decomposition than bogs. However, even relatively low average accumulation rates can eventually lead to a large accumulation of peat over long periods of time. While long-term average accumulation rates can be inferred from examining peat profiles through radionuclide dating procedures, incremental values are more difficult to infer since the rate of composition of the peat is variable and the accuracy of various current methodologies for dating recent ($<$ 200 years) deposits has not been proven.

The concept that essentially all peat litter decomposition occurs in the upper, aerobic peat layer is not valid. Although decomposition rates generally decline with increasing depth, some alterations occur at depth, and given the long periods of peat residence, these processes cannot be ignored (Clymo, 1983).

Major variables influencing decomposition/accumulation rates are:

- seasonal changes in chemical reaction rates and rates of biological metabolism
- type of plant species and plant parts contributing litter (susceptibility to breakdown and antibiotic properties)
- stage of decomposition (there is a slowdown in decomposition rate as litter becomes increasingly decomposed)
- water chemistry
- variations in water level
- microtopographic relief factors (influencing degree of litter aeration, susceptibility to inundation, erosion, rates of horizontal and vertical water flow)
- meteorological alterations (long- and short-term) temperature, precipitation and their influence on surface versus subsurface decay rates
- vegetation profile (roots of some species promote decomposition by growing through litter particles, or by indirectly promoting microbial activity)
- partial pressure of gases.

Tallis (1983) reviewed data on accumulation rates and concluded that, longterm peat accumulation may range from less than 1% to 52% of NPP. McKee and Rowsell (1983) estimated a value for a hypothetical bog in northwestern Ontario where accumulation was 18.3% of NPP, based on characteristics of ombrotrophic bogs as reported by Graham (1979). More experimental data are needed for Canadian peatlands to permit adequate model simulation of these processes. Table 10 summarizes some of the existing data.

Decay rates in peatlands are frequently given in terms of a "rate of loss constant" - the fraction of accumulated peat which decays per unit time. Estimates of this value for blanket bog peat (from a mathematical model) are 10^{-3} to 10^{-5}/year (Clymo, 1978).

TABLE 10: PEATLAND LITTER ACCUMULATION AND DECOMPOSITION RATES

Site	Dominant Vegetation or Peatland Type	Peat and Type	Annual Accumulation Rate	Decomposition Rate	Comments	Reference
Moor House, U.K.	Blanket bog	bog				Clymo & Reddaway 1971
	Sphagnum hummocks		1.0 g/dm^2		42% of NPP	
	Sphagnum pools		1.8 g/dm^2		52% of NPP	
	Sphagnum lawns		2.7 g/dm^2		71% of NPP	
Northern U.K.	lowland poor fen	fen		20% in first year	top 10 cm	Clymo 1965
	upland blanket bog several Sphagnum spp. in litter bags	bog		5% in first year	at 75 cm	
	blanket bog filter paper			3%/year	at 75 cm	Clymo 1965
	blanket bog	bog				Heal and French 1974
	Narthecium, Rubus leaves			45% in first year	Prior to	
	Calluna stems			10% in first year	abscission	
	blanket bog	bog				Latter and Cragg 1967
	Juncus squarrosus leaves			30% OM/27 mo.	L&F layers	
	blanket bog	bog				Clymo & Reddaway 1971
	Sphagnum spp.			15% OM	leaching loss	
				85% OM	gaseous loss	
	fen	fen				Mason & Bryant 1975
	Phragmites leaves			1.4 years	100% decomp.	
	Typha leaves			2.1 years	100% decomp.	
(not given)	drained raised bog	bog				Frankland 1966
	Pteridium petioles			40% OM in 5 years		
Colorado	fibrous or Sphagnum peat		1.8, 1.9, 3.2, 9.6 cm/100 years			Pennak 1963
Minnesota	fibrous or Sphagnum peat		4.6, 5.0, 13.6 cm/100 years			Heinselman 1963, 1970
NWT, Canada	fibrous or Sphagnum peat		1.7, 2.9, 3.0, 3.6 cm/100 years			Nichols 1967
Washington			3.7 cm/100 years			Rigg & Gould 1957
Mean of 12 Values	fibrous or Sphagnum peat		4.5 cm/100 years			Tallis 1983
Central Alberta			0.55 cm/ 50-60 g/m^2			Zoltai and Johnson 1983
(not given)			30 cm/300 years			Caron 1980

However, decay rates vary considerably with regard to the set of factors listed above, and may encompass up to 4 or 5 orders of magnitude when comparing unsaturated versus saturated zone decay rates (Clymo, 1983).

Coulson and Butterfield (1978), using the litter bag technique, reported near-surface rates for selected parts of peatland plant species. Variation of one or more orders of magnitude in the rate of loss constant may be inferred if a highly decay-resistant Sphagnum species is included. Rate of weight loss during one year ranged from 0.14 to 0.78 for various species. Other experiments of a similar nature but including other species' plant parts (including roots and leaves) give annual ranges of 0.01 to 0.45 (Heal et al., 1978) and 0.08 to 0.16 (Clymo, 1965).

Several workers have determined the rate of oxygen consumption in peatland litter with respect to varying temperature and moisture regimes. Oxygen consumption may be assumed to be an indirect measure of decay. A range of one to two orders of magnitude was determined by Rosswall (1974) and others, in dealing with a temperature range of $-5^{o}C$ to $30^{o}C$. With increased temperature, water content has a strong influence on decay rate. For example, oxygen consumption in peat at $8^{o}C$ and 320% water content is double that at $8^{o}C$ and 20% water content (Flanagan and Bunnell, 1976).

The nutrient content of plant matter appears to influence the rate of decay as well. Fertilization experiments by Coulson and Butterfield (reported by Clymo, 1983) indicated that the decay rate of the same plant species was greater if the plants had been grown on a nitrate fertilized peatland. However, the decay rate change was less than one order of magnitude.

Of considerable importance is the effect of water table depth on decay rates. In most Canadian peatlands the water table fluctuates seasonally. Depending on its position, surface leaching and oxygenation combine with moisture content and other factors to determine the decay rate. However, despite the interactive nature of the driving mechanism of decay, an abrupt decrease in decay rate is generally observed at the water table. Clymo (1965) reported an abrupt decline in the decay rate of less than one order of magnitude compared to the decay rate in peat immediately above the water table but a decline of approximately one order of magnitude compared with the surface decay rate.

In summary, although decay rates in the saturated zone of peatlands are probably too low to accurately measure by standard methods now in use, Clymo (1983) speculates that they are perhaps 100 times lower than in the unsaturated zone, taking into consideration the numerous influential factors mentioned above.

3.3 Chemical Composition and Dynamics

Peatland biota store and transmit many chemical elements and compounds. While the chemical composition of peat has been studied extensively (Section 5.0), the composition of the plants which form peat have not. Data of this type are required to model flux rates in peatlands. Net primary productivity and litter production/decay rates can be used in combination with elemental composition, to determine fluxes to other environmental compartments. Care must be exercised, however, in inferring that the composition of litter is the same as that of living matter. Certain processes which occur during the senescence and decay stages make this assumption untenable for many chemical species.

The experimentally determined quantities of elements and molecular compounds in biotic tissue relate to the sampling and analytical methods used. No attempt is made here to assess the comparative extraction efficiency or other qualifiers. Data specific to a number of these elements and to various peatland species are presented in Table 11.

3.3.1 Nutrients

3.3.1.1 Nitrogen

In bogs, nitrogen bioavailability may be limited by the virtual absence of a minerotrophic water supply and the inhibition of nitrogen fixation by aerobic bacteria as a result of low pH (Dickinson, 1983). Similarly, many genera of N-fixing blue-green algae prefer neutral to alkaline conditions, while symbiotic N-fixing organisms, such as Rhizobium appear poorly adapted to bog conditions because of low pH, and high concentrations of soluble metal ions (Holding and Lowe, 1971). Other types of symbiotic organisms are associated with roots of several common fen and swamp plants, although nutrient dynamics in these ecosystems is not as well understood. For example, Alnus and Myrica have root nodule associated actinomycetes.

TABLE 11: SPECIFIC PEATLAND PLANT CHEMICAL CONSTITUTION

Species	N % Mean Content	P % Mean Content	K % Mean Content	Na mg/g	Ca mg/g	Mg mg/g	Al mg/g	Mn mg/g
A. BOG EVERGREENS								
Ledum groenlandicum Oeder	1.41	0.086	0.64					
Chamaedaphne calyculata (L.) Moench	1.36	0.080	0.39					
Andromeda glaucophylla Link	1.14	0.063	0.58					
Kalmia angustifolia L.	1.22	0.072	0.49					
Kalmia polifolia Wang.	1.30	0.070	0.47					
Sarracenia purpurea L.	1.09	0.085	0.47					
Picea mariana (Mill.) BSP	1.02	0.086	0.59					
Mean	1.22	0.077	0.52					
Standard Error of Mean	0.044	0.0034	0.020					
Bog Deciduous								
Aronia melanocarpa (Michx.) Ell.	1.74	0.139	1.06					
Gaylussacia baccata (Wang.) K. Koch	1.66	0.083	0.68					
Vaccinium myrtilloides Michx.	1.54	0.070	0.36					
Larix laricina Mill.	1.28	0.080	0.68					
Betula pumila L.	1.81	0.105	0.47					
Betula populifolia Marsh	1.79	0.095	0.55					
Nemopanthus mucronata (L.) Trel.	1.62	0.100	1.03					
Viburnum cassinoides L.	2.08	0.106	0.73					
Mean	1.69	0.097	0.70					
Standard Error of Mean	0.077	0.0025	0.085					
Non-Bog Evergreens								
Picea glauca (Moench) Voss	1.41	0.103	0.83					
Pinus strobus L.	1.22	0.098	0.58					
Thuja occidentalis L.	1.28	0.128	0.58					
Mean	1.30	0.110	0.66					
Standard Error of Mean	0.03	0.0134	0.057					
Non-Bog Deciduous								
Spirea alba du Roi	2.08	0.112	0.72					
Spirea tomentosa L.	1.86	0.138	0.81					
Acer rubrum L.	2.11	0.093	0.46					
Alnus rugosa (du Roi) Spreng.	2.53	0.101	0.81					
Rubus hispidus L.	2.02	0.123	1.15					
Salix fragilis L.	2.66	0.238	1.09					
Ulmus americana L.	1.94	0.143	0.72					
Comptonia peregrina (L.) Coult.	2.21	0.077	0.65					
Populus tremuloides Michx.	1.94	0.089	1.13					
Ilex verticillata (L.) Gray	2.53	0.097	1.38					
Mean	2.19	0.126	0.89					
Standard Error of Mean	0.088	0.0161	0.085					
Reference: Small (1972)								
Location: Mer Bleu Bog, Ontario								
B. CENTRAL BOG								
Sphagnum magellanicum	0.98	0.084	0.35	0.59	0.94	0.49	0.43	0.10
Eriophorum vaginatum	0.98	0.080	0.61	0.14	0.85	0.90	-	0.20
Calluna vulgaris	1.02	0.069	0.40	0.47	2.9	1.23	0.12	0.31
Erica tetralix	0.82	0.048	0.29	0.67	3.2	0.86	0.24	0.46
Mean	0.95	0.070	0.41	0.47	1.97	0.87	0.26	0.39
Sphagnum fuscum bog hummock	0.911	0.035	0.343	0.50	1.31	0.54	0.20	0.28
Pinus silvestris slope	1.35	0.078	0.039	0.19	1.77	0.82	1.19	0.067
Reference: Damman 1978								
Location: Taneroas Mosse, Sweden - 56°09'N/13°19'E								
C. WETLAND SPECIES								
Sedges (6 Carex spp.)								
May	1.97	0.16						
June	1.71	0.12						
July	1.36	0.10						
August	1.22	0.09						
Mean	1.26	0.12						

TABLE 11: SPECIFIC PEATLAND PLANT CHEMICAL CONSTITUTION (cont'd)

Species		N % Mean Content	P % Mean Content	K % Mean Content	Na mg/g	Ca mg/g	Mg mg/g	Al mg/g	Mn mg/g
Willows (4 Salix spp.)									
Leaves:	May	3.37	0.33						
	June	2.36	0.22						
	July	2.21	0.14						
	August	2.00	0.12						
	Mean	2.48	0.20						
Stems (new):	July	0.87	0.11						
	August	0.86	0.09						
	Mean	0.87	0.10						
Stems (old):	May	0.68	0.06						
	June	0.62	0.06						
	July	0.55	0.05						
	August	0.55	0.05						
	Mean	0.60	0.06						
Bog Birch (Betula pumila)									
Leaves:	May	3.49	0.30						
	June	2.41	0.15						
	July	2.06	0.11						
	August	1.87	0.09						
	Mean	2.46	0.16						
Stems (new):	June	2.17	-						
	July	1.24	0.10						
	August	0.90	0.07						
	Mean	1.44	0.08						
Stems (old):	May	0.65	0.04						
	June	0.69	0.05						
	July	0.57	0.05						
	August	0.57	0.04						
	Mean	0.62	0.04						
Leatherleaf (Chamaedaphne calyculata)									
Leaves (new):	June	2.59	0.22						
	July	1.88	0.10						
	August	1.71	0.09						
	(Mean)	2.06	0.14						
Leaves (old):	May	1.83	0.12						
	June	1.76	0.10						
	July	1.50	0.07						
	August	1.33	0.07						
	Mean	1.60	0.09						
Stems (new):	June	1.92	-						
	July	0.99	0.10						
	August	0.71	0.07						
	Mean	1.21	0.08						
Stems (old):	May	0.56	0.04						
	June	0.55	0.04						
	July	0.44	0.04						
	August	0.44	0.03						
	Mean	0.50	0.04						
Reference: Richardson et al. (1978)									
Location: Houghton Lake, Michigan									
D. FENS AND SWAMPS									
Larix laricina foliage									
fen (August)		1.95	0.26			0.52	0.19		
conifer swamp (August)		1.06	0.25			0.42	0.14		
bog (August)		1.24	0.17			0.37	0.09		
Reference: Tilton (1977)									

TABLE 11: SPECIFIC PEATLAND PLANT CHEMICAL CONSTITUTION (cont'd)

Species	Pb mg/kg	Zn mg/kg	Cu mg/kg	As mg/kg
E. BOG				
Sphagnum fuscum bog hummock	19.2	38.7		
Pinus silvestris slope	91.9	91.7		
Reference: Damman (1978)				
Location: Tanerods Mosse, Sweden - 56°09'N/13°10'E				
F. MIXED BOG (MEANS)				
Eriophorum vaginatum				
Leaves	18.1	107		
Leaf bases	93.4	65.5		
Calluna Vulgaris				
Green shoots	19.2	49.3		
Old shoots	57.5	49.5		
Sphagnum papillosum				
1-2 years old	12.1	11.4		
3-4 years old	12.4	37.7		
Low background sites (Mean)				
Ombrogenous sites	57 (10)[a]	116 (4)	12.6 (10)	
High background sites (mean)				
Ombrogenous sites	320 (5)	141 (4)	49.2 (4)	
G. MIRES				
Site 2 (South Finland)	30			
Site 3 (South Finland)	20			
Site 4 (South Finland)	21			
Site 5 (South Finland)	20			
Site 6 (South central Finland)	12			
Site 8 (North Finland)	7			
Site 9 (North Finland)	5			
Site 10 (North Finland)	6			
Data approximate, inferred from histograms.				
References: Pakarinen & Tolonen (1977)				
H. BOGS				
Sphagnum fuscum:	minimum			0.16
	maximum			0.40
Chamaedaphne calyculata:	minimum			0.03
	maximum			2.3
Cladonia:	minimum			0.11
	maximum			0.32
Ledum groenlandicum:	minimum			0.03
	maximum			0.07
References: Arafat & Glooschenko (1982)				
Various sites in northern Ontario, both near and distant from metal smelting as sources.				
I. MOSSES				
Range	minimum			0.0
	maximum			0.2
References: Furr et al. (1979)				
Location: Adirondack Mountains, New York				

[a] number of samples

Several classes of fungal mycorrhizal associates, which permit increased plant root N uptake and uptake of other nutrients, have been identified with several important families of peatland plants (Table 12). However, in peatlands, unlike many other terrestrial ecosystems, green plants appear to obtain nutrients without the intervention of microorganisms, although this conclusion requires more complete documentation (Dickinson, 1983). Figure 6 provides a preliminary summary of the nitrogen cycle in an ombrotrophic bog.

Green plants retain the majority of N in proteinaceous compounds. There appears to be relatively little difference in this regard with comparison to non-bog plants (Small, 1972), but the concentration of N, in non-bog plants appears to be frequently higher than in bog plants (Table 11). By applying typical N concentrations to species biomass values, total nitrogen inventories may be derived.

Several vegetation-related processes influence nitrogen cycling rates. Many bog plants appear to reabsorb significantly more nitrogen from senescent parts prior to their abscission. In a representative Ontario bog, Small (1972) calculated the potential photosynthate which several species could manufacture during the time a given unit of N remained in the plant prior to litterfall. In bog evergreens, this figure was 235% higher than for bog deciduous plants and 60% higher in the latter than in non-bog deciduous species. Thus, at least some bog plants reduce their N requirements by retaining it selectively. This has implications for other fluxes and for litter inventory. Some plants (e.g., Sarracenia purpurea and Drosera spp.) are carnivorous and are able to obtain nitrogen from their prey.

Fixation of atmospheric nitrogen by microflora appears to be a major source of nitrogen input to peatlands. In a study of Thoreau's Bog (Massachusetts), Chapman and Hemond (1982) estimated that the annual rate of dinitrogen fixation was 1.0 gN/m^2 as compared to a precipitation input rate of 0.7 gN/m^2. Other data sources, listed in Table 13, demonstrate the frequently higher rate of nitrogen fixation in richer minerotrophic peatlands. There do not appear to be any relevant data for Canadian peatlands.

Several groups of microflora are also responsible for nitrogen mediating activities in peatlands. They include: free-living aerobic, facultative and anaerobic bacteria (N fixers); free-living and semi-symbiotic blue-green algae (N fixers); symbiotic Rhizobium

TABLE 12: OCCURRENCE OF MYCORRHIZAL ASSOCIATIONS OF PEATLAND PLANTS

Type of Mycorrhizal Association	Higher Plant Partner Examples	
	Family	Species
Ectomycorrhizal	Myrtaceae	Eucalyptus spp.
	Pinaceae	Pinus spp.
	Betulaceae	Betula pubescens
Ericoid	Empetraceae	Empetrum nigrum
	Ericaceae	Andromeda polifolia
		Calluna vulgaris
		Erica cinerea
		Erica mackaiana
		Erica tetralix
		Vaccinium myrtillus
		Vaccinium oxycoccos
		Vaccinium vitis-idaea
Arbutoid	Ericaceae	Arctostaphylos uva-ursi
Arbuscular	Cyperaceae	Carex stans
		Kobresia sp.
	Liliaceae	Narthecium ossifragum
	Poaceae	Molinia caerulea
		Nardus stricta
Orchidaceous	Orchidaceae	Liparis loeselii
		Listera cordata
		Malaxis paludosa
		Orchis fuchsii
		Spiranthes romanzoffiana
No associations found to date	Cyperaceae	Cladium mariscus
		Eriophorum vaginatum
		Schoenus nigricans
	Juncaceae	Juncus squarrosus
	Poaceae	Phragmites australis
	Menyanthaceae	Menyanthes trifoliata
	Nymphaeaceae	Nuphar lutea
		Nymphaea spp.
	Rosaceae	Rubus chamaemorus

Source: Dickinson (1983)

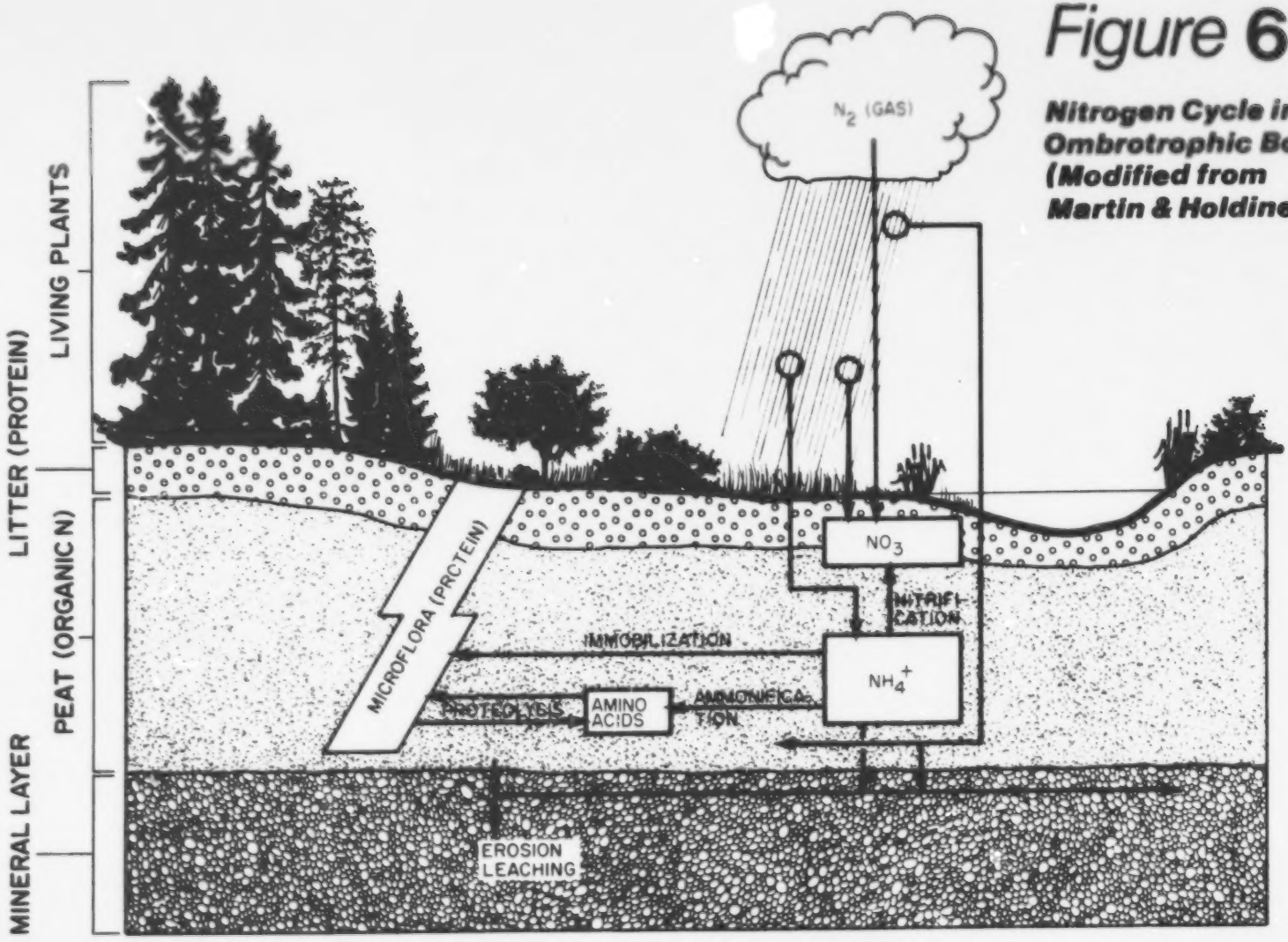


Figure 6

Nitrogen Cycle in an Ombrotrophic Bog (Modified from Martin & Holdine 1984)

TABLE 13: SUMMARY OF ANNUAL RATES OF NITROGEN FIXATION IN PEATLANDS

Investigator	Location	Peatland Classification	Major Vegetation	Organism and Relationship	Annual Rate Nitrogen Fixation $g\ N.m^{-2}.year^{-1}$
Granhall and Selander, 1973	Sweden	Subarctic mire Ombrotrophic	Andromeda sp. - Eriophorum - Sphagnum fuscum	Anaerobic bacteria in peat (0-5 cm depth)	0.03
		Ombrotrophic	Andromeda sp. - Eriophorum - Sphagnum fuscum	Aerobic bacteria in surface peat	0.15
		Minerotrophic	Eriophorum - Carex - S. riparium	Moss surrounded by blue-green algae in surface wet depressions	0.16
		Minerotrophic	Eriophorum - Carex - Drepanocladus	Moss with epiphytic and (or) intracellular blue-green algae in wet depressions	9.4
		Minerotrophic	Eriophorum - Carex - Drepanocladus	Free living blue-green algae in pools	11.5
Basilier, Granhall and Stenstrom, 1978	Sweden	Minerotrophic	Eriophorum - S. riparium		1.0-6.4
			Eriophorum - S. riparium	Mosses associated with green algae	9.4
Waughman and Bellamy, 1980	Southern Germany	Rich fen	Sphagnum spp.	Heterotrophic bacteria in aerobic portions of peat	6.0
		Intermediate fen	Sphagnum spp.	Heterotrophic bacteria in aerobic portions of peat	2.1
		Poor fen	Sphagnum spp.	Heterotrophic bacteria in aerobic portions of peat	0.53
		Ombrotrophic bog	Sphagnum spp.	Heterotrophic bacteria in aerobic portions of peat	0.07
Chapman and Hemond, 1982	Massachusetts, U.S.A.	Ombrotrophic	Chamaedaphne - Sphagnum spp.	Aerobic surface peat organisms	1.0

(N fixers); symbiotic actinomycetes (N fixers); phycobiont blue-green algae (N fixers); mycorrhizal fungi (facilitate plant uptake of ammonium and other forms of N, can enzymatically degrade complex N compounds, and tannins and effect an increase in local pH; possibly also supply carbohydrate to plants); and, rhizosphere organisms (Granhall and Selander, 1973; Blasco and Jordan, 1976; Basilier et al., 1978; Waughman and Bellamy, 1980).

3.3.1.2 Phosphorus

Phosphorus is frequently mentioned in conjunction with nitrogen as a nutrient which limits plant production in peatlands. The relative importance of the one as opposed to the other appears unclear. It is possible that either or both simultaneously limit productivity but generalization as to their relative importance in any type of peatland (bog, fen or swamp) does not appear possible. The total inventory of phosphorus in peatland ecosystems is strongly dependent on the organic matter which binds it. Bioavailability depends primarily on the concentration of inorganic forms.

Within peatland plants, there appears to be lower total concentrations of P in bog versus fen plants (Waughman, 1980). However, bioavailable phosphorus in peat may be lower in fens than bogs (Section 5.3.2).

Green plants contain a large quantity of phosphorus relative to the surface litter layer (Richardson et al., 1978). Concentrations of the element in actively growing peatland plants do not appear to be greatly different from upland plants but total inventory is much less due to the lower biomass and productivity values. Plants endemic to acid bogs appear to have certain adaptations which lead to a conservancy of certain nutrients and/or to a tolerance to lower nutrient availability (Small, 1972). Typical concentrations in peatland plants are given in Table 11. The range reflects the biomass. Insofar as fens and swamps are more productive than bogs and (usually) contain greater stores of biomass, phosphorus inventory is greater.

Phosphorus input to vegetation occurs via precipitation, ground water and recycling within the litter and root layers. Richardson et al. (1978) have reviewed some of the literature concerning phosphorus dynamics in peatlands, but it is difficult to compare various peatland classes as to relative quantities of phosphorus cycled among

compartments. Nevertheless, considerable efflux of phosphorus from peatlands is implicated, mainly as losses in stream flow (resulting from litter formed by the biota). There is evidence that phosphorus dynamics in peatlands involves a tight balance between input and output (precipitation and stream outflow) and that disturbances such as erosion or fertilization will lead to fairly rapid increases in outflow concentrations (Burke, 1975).

3.3.1.3 Potassium

Potassium is implicated in both the ion exchange process involving both organic and inorganic sites, as well as the nutrition of peatland plants. This element is bioconcentrated in vegetation at levels up to or more than five or six times the concentration in underlying peat. Concentrations appear to be generally lower in bog plants than in fen plants (Table 11) (Waughman, 1980). However, extractable K appears to be lower in at least some fens than in bogs.

Although nitrogen and phosphorus are usually indicated as the major productivity-limiting nutrients in peatlands, potassium may in some cases be the limiting nutrient (Goodman and Perkins, 1968).

3.3.2 Trace Elements

Trace element concentrations in peatland vegetation are highly variable, and depend on precipitation chemistry, groundwater influence and bioconcentration potential of individual plant species. Sphagnum and other bog species have long been recognized as indicators of atmospheric pollution, since they obtain most of their nutrients from precipitation input (Pakarinen and Tolonen, 1977; Damman, 1978; Arafat and Glooschenko, 1982).

4.0 PHYSICAL PROPERTIES OF PEAT

Physical characteristics form the basis of organic soil classifications in both the Canadian and American systems, and are a component of the proposed International Peat Society Classification of Commerical Peats (Table 14; U.S. Soil Conservation Service, 1973; Canadian Soil Survey Committee, Subcommittee on Soil Classification, 1978). They are important, from both ecological and technological perspectives, in that they directly control two key hydrological characteristics; water retention capacity and hydraulic conductivity. Most routinely measured physical properties of peat are indicators of decompositional state. These include:

- o von Post scale
- o bulk density
- o fiber content
- o colour
- o ash content
- o pyrophosphate index

While statistically significant intercorrelations exist between all of these parameters, the three considered to be the most reliable indicators of decompositional state are; von Post scale, bulk density and fiber content (Figure 7). For the purposes of mathematical modelling, the latter two are favoured since they are based on relatively standardized analytical methodologies.

4.1 Bulk Density

Bulk density measures decomposition on a volumetric basis. It is defined as the weight of a given volume of soil (Brady, 1974). This includes the volume occupied by pore space as well as solid particles. The relationship of bulk density to decomposition is illustrated in Figures 7a and 7b. Living plants contain large volumes of cellular pore space. During the decomposition process, bio-oxidation and other chemical reactions cause a breakdown of cellular structure, resulting in a gradual compression of the plant. Thus, volume is reduced as decomposition proceeds, and bulk density increases.

The dry bulk density of peat is approximately 75-85% less than that of mineral soils, typically ranging between 0.01 - 2.0 g/cm^3 (Paivanen, 1969; Puustjarvi, 1977; Levesque et al., 1980). This means that approximately 85-97% of a unit volume of peat is occupied by pore space, which can be filled with air (gas) or water. The high field moisture

TABLE 14: OUTLINE OF A COMMERCIAL CLASSIFICATION OF PEATS
(Kivinen, 1977)

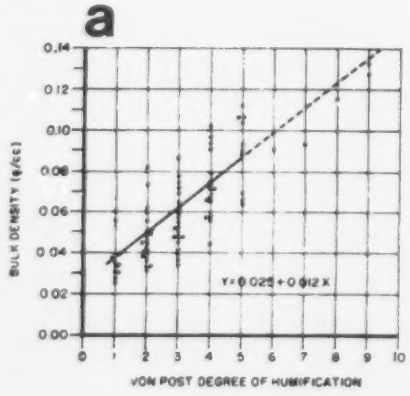
Three characteristics are used:

1. Botanical composition
   (a) moss peat: 75% moss, 10% wood
   (b) herbaceous peat: 75% herbaceous plants, 10% wood
   (c) wood peat: 35% wood
   (d) mixed peat: any other type

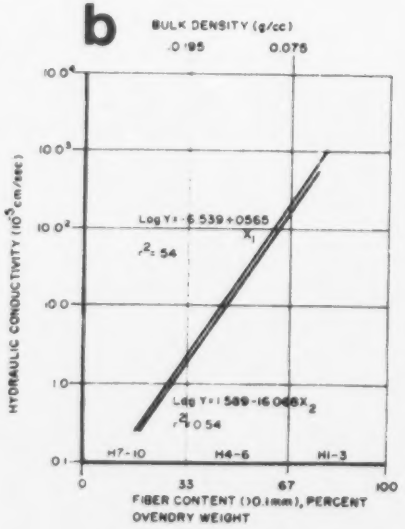
2. Decomposition
   (a) little decomposed
   (b) medium
   (c) highly decomposed

3. Nutritional state
   (a) oligotrophic
   (b) mesotrophic
   (c) eutrophic

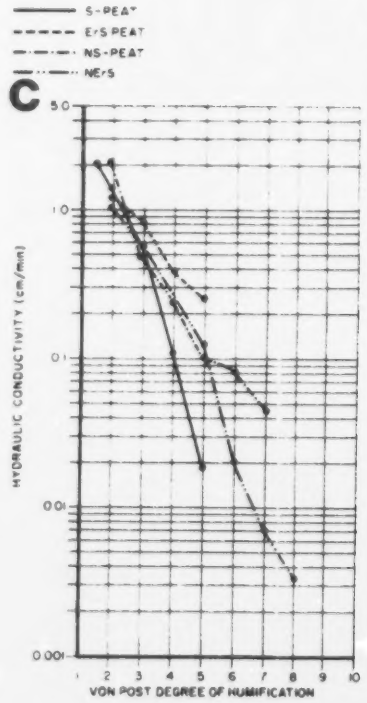
This scheme is the basis for the proposed International Classification.



BULK DENSITY VS. DECOMPOSITION
(Korpijaakko & Radforth, 1972)



INTERRELATIONS OF PHYSICAL PROPERTIES OF PEAT AND CORRELATION WITH HYDRAULIC CONDUCTIVITY
(Boelter, 1969)



DEGREE OF HUMIFICATION VS HYDRAULIC CONDUCTIVITY FOR VARIOUS TYPES OF PEAT

S= Sphagnum
E=Eriophorum
N=Shrub
(Korpijaakko & Radforth, 1972)

FIGURE **7**

Relationships Between Physical Properties of Peat and Hydraulic Conductivity

content, typically associated with peat, indicates that water predominates in the pores. Significant differences in bulk density are observed between peats of different botanical origins. These are related to the degree of resistance of the cellular structure to biodegradation. Sphagnum-dominated peats typically display lower bulk densities (0.02 - 0.11 g/cm^3) than sedge peats (0.12 - 0.14 g/cm^3). Bulk densities of peat from a variety of peatland types and geographical locations are displayed in Table 15.

4.2 Fiber Content

Decomposition may also be defined by the size distribution of the peat particles. The rationale here is that as the peat decomposes the size of the plant fibers decreases. Consequently unhumified peats have higher fiber contents than humified peats (Table 15). Fiber content is conventionally defined as the percentage of peat material composed of particles greater than 0.1 - 0.15 mm in length. Fibers of this size retain recognizable characteristics of the original plant material (Levesque and Dinel, 1977).

Dinel and Levesque (1976) show that mechanical separation of peat into particle size classes ranging from $<$ 0.07 - 2 mm is also a reliable indicator of the state of decomposition. In addition the distribution of particle size fractions appears to relate well to botanical composition and chemical properties such as mineral content and cation exchange capacity.

4.3 von Post Scale

The von Post scale of humification has been the standard field test of decomposition since the early 1900's (von Post, 1921). This system utilizes recognizable features of the plant remains, and the amount and colour of water released by squeezing to determine relative decomposition on a scale of 1-10. Von Post humification ratings can be correlated with bulk density or fiber content (Figures 7a and 7b), and represent a convenient qualitiative method for differentiating horticultural peat (H2-4) from fuel peat (H3-10).

TABLE 15: PHYSICAL PROPERTIES OF PEAT

Location	Peatland Type	Depth Range	Decomposition	Bulk Density	Fiber Content	Hydraulic Conductivity
New Brunswick:						
Central (Bog No. 41)	Sphagnum	0-120 120-360	H1-3 H4-5	0.06 0.04-0.07		
Coastal (Bog No. 573)	Sphagnum with sedge-shrub lenses	20-350 350-	H3 H6			
Western (Bog No. 731)	Sphagnum	200-530	H3-6	0.06-0.10		
(New Brunswick DNR, 1983)						
Nova Scotia:						
Queens Co. (Bog No. Q1204)	Sphagnum	0-370	H3-7	0.120-0.510		
Hants Co. (Bog No. 12104)	Sphagnum	0-410 410-650	H2-4 H4-7	0.060-0.120 0.105-0.175		
Southwestern Nova Scotia (Bog No. U812)	Sphagnum	0-10 10-400	H2 H4-8	0.080 0.100-0.515		
(Nova Scotia Dept. Mines, 1983)						
Quebec:						
Farnham (Levesque et Millette, 1977)		0-15 15-30 30-45 45-60 60-75 75-105			37.5 20.9 20.1 18.3 14.6 14.1	
St. Clothilde Ormstown Gatineau Park (Levesque et Dinel, 1977)	woody forest peat sedge Sphagnum				42.1 29.6 65.6	
Farnham Ormstown St. Chrysostome Clair St. Charles (Levesque et Dinel, 1982)	Fen-woody fen Bog-sedge Swamp (woody forest) Bog (Sphagnum)	65-75 85-92 65-85 30-40		0.115 0.114 0.131 0.68	8.6 23.3 34.0 59.3	

TABLE 15: PHYSICAL PROPERTIES OF PEAT

Location	Peatland Type	Depth Range	Decomposition	Bulk Density	Fiber Content	Hydraulic Conductivity
Minnesota	Sphagnum	0-30	Fibric	0.015 - 0.075	70-98	1.5×10^{-3}
(Boelter, 1965, 1969;		30-45	Hemic	0.08 - 0.19	40-45	$1.5 \times 10^{-3} - 1.2 \times 10^{-5}$
Boelter and Verry, 1977)		45-60	Sapric	0.21 - 0.26	15-30	1.2×10^{-5}
	reed/sedge	60-100	Hemic	0.12 - 0.17	40-45	$1.5 \times 10^{-3} - 1.2 \times 10^{-5}$
Finland	Sphagnum		H1	-0.053		
(Puustjarvi, 1977			H2	0.053 - 0.068		
in Monenco, 1981)			H3	0.68 - 0.083		
			H4	0.083 - 0.098		
			H5	0.098 - 0.113		
			H6	0.113 - 0.128		
			H7	0.128 - 0.143		
			H8	0.143 - 0.158		
			H9	0.158 - 0.173		
			H10	0.173-		
Germany						
Baden and Eggelsmann, 1963			H3			5.8×10^{-2}
			H3-H5			$5.8 \times 10^{-2} - 1.2 \times 10^{-2}$
			H5-H8			$1.2 \times 10^{-2} - 2.3 \times 10^{-3}$
			H8			2.3×10^{-3}
Norway		30	H5-H6			2.9×10^{-2}
Nilssen, 1978		50	H6			1.1×10^{-2}
(laboratory method)		70	H6			1.6×10^{-3}

4.4 Hydraulic Conductivity

Hydraulic conductivity expresses the dynamic aspects of soil-water relations. It is defined as the velocity of flow across a unit area of peat in response to a hydraulic gradient.

In bogs, hydraulic conductivity exerts a direct control on infiltration rate, and the amount of water available for plant uptake or evapotransiration. In minerotrophic systems, hydraulic conductivity influences groundwater movement. Indirect effects include regulation of plant root aeration and nutrient availability (Rycroft et al., 1975).

Hydraulic conductivity has both horizontal and vertical components, although generally only the latter is measured. The vertical component is most often associated with water table fluctuations, while the horizontal component is dependent on the pressure head gradient between two locations (Dai and Sparling, 1973; Ingram, 1983). The relative importance of each component is unclear. Dai and Sparling (1973) found that Sphagnum bogs in northeastern Ontario had a larger vertical component and smaller horizontal component than sedge fens. However, Boelter (1965) found no difference in vertical or horizontal conductivity within each of four Minnesota peats tested.

Nonetheless characteristic differences in (vertical) hydraulic conductivity are observed between peats. These can be related to botanical origin and decompositional state, depth within the profile and compaction (Figure 7a and 7b). Peat exhibits a much wider variation in hydraulic conductivity than mineral soils, typically ranging up to 8 cm/sec in surface vegetation, to 10^{-1} - 10^{-3} cm/sec in Sphagnum-dominated surface layers, to 10^{-6} cm/sec in highly humified layers (Boelter, 1970; Korpijaakko and Radforth, 1972; Rycroft et al., 1975). Comparable values for mineral soils are 10^{-2} - 10^{-3} cm/sec for sandy loam or fine sand, and 10^{-5} - 10^{-6} for clays (Brady, 1974).

Most peat profiles exhibit a decrease in hydraulic conductivity with depth in response to increasing decomposition and compaction. Wechmann (1943) showed that hydraulic conductivity decreased from 1×10^{-6} cm/sec to 3×10^{-9} cm/sec in a humified Sphagnum peat as the surface load was increased from 400 - 2,000 kg/m^2.

Water movement within a saturated peat profile follows Darcy's Law as a general rule:

$$Q = -K \frac{\Delta H}{I} \qquad \text{or} \qquad K = -Q \frac{I}{\Delta H}$$

Where, Q = volume flux
K = rate of movement (hydraulic conductivity)
Δ H = hydraulic head
I = distance

Anomalous situations have, however, been reported. Dai and Sparling (1973) and Ingram et al. (1974) found that field measurements of hydraulic conductivity obeyed Darcian Law for non-humified peats, but varied with hydraulic head in humified peat. The latter result contradicts Darcy's Law, which defines hydraulic conductivity as a proportionality constant. Galvin and Hanrahan (1967) reported a similar pattern in laboratory tests, which they attributed to increased pore pressure resulting from air entrapment. Since the bulk of the literature supports Darcian Law for water movement in all types of peats it would appear that these anomalous findings may arise from sampling error, or are restricted to site-specific situations. Recent studies (Hemond, 1984, pers. comm.) have shown that apparent non-Darcian transport may be explained by the inclusion of a water storage function in the flow equation.

4.5 Water Retention Capacity

The ability of the peat to retain water affects storage potential and water yield characteristics. Water retention capacity is directly related to physical properties of the peat such as bulk density, fiber content and porosity (Boelter, 1969; Puustjarvi, 1977). In general, highly decomposed peats with small pore spaces are able to retain more water for longer periods of time, through matric and surface forces, than loose unhumified peats. Actual moisture content is highly variable and is dependent upon the net amount of water input to the system and mechanical properties of the peat, i.e., compaction, shear strength. As described in Section 2.0, the catotelm is the major water storage unit of the peatland.

5.0 PEAT CHEMISTRY

Chemical factors have been recognized as major influences on peatland ecology since the early 1900's (e.g., Godwin, 1931; Sjors, 1950; Gorham, 1957; Heiselman, 1970). Sjors (1961) and Gorham (1967) were among the first to conclude that water entering peatlands from different sources had significantly different chemical compositions. Confirmation of this by studies in a variety of peatland types and geographic locations lead to the widespread recognition of ombrotrophic and minerotrophic peatlands, commonly defined on a chemical basis by pH, calcium concentration or specific conductivity:

	Ombrotrophic (Bogs)	Minerotrophic (Fens, Swamps)
pH	3-4	4-8
Specific Conductivity	80 umhos/cm	100 umhos/cm
Calcium	4-5 mg/L	5 mg/L

However, water source did not explain the observed local and seasonal variability in peat water chemistry. Subsequently, peat was recognized as a highly chemically reactive compound which exerts strong influences on water chemistry. Seasonal growth stage and rooting depth of surface vegetation were also shown to modify local water quality (Summerfield, 1974; Tervet, 1976).

The following sections describe chemical parameters or compounds considered to be of ecological or environmental importance in peatlands, and examine the interactions which affect their behaviour.

5.1 Organic Composition of Peat

The progressive transformation of living plant tissue into peat is a complex process involving solubilization and removal of some substances and formation of others, through chemical and biologically-mediated reactions. The chemical composition is dynamic, and relative concentrations of organic compounds which comprise peat at a given point in time are dependent upon botanical origin, humification, depth and age (Clymo, 1983).

Hundreds of specific compounds may be isolated through fractionation procedures. However, all are combinations of carbon, hydrogen, oxygen, nitrogen and sulphur. On a dry weight basis carbon and oxygen are the dominant elements. Relative proportions increase and decrease, respectively, during the decomposition process (Table 16a).

Six to eight groups of organic compounds are typically represented in descriptions of peat composition. These include cellulose, hemicellulose, proteinaceous nitrogen compounds, lignins, bitumens and humates. Relative percentages change as decomposition and humification progress (Table 16b); in general, plant tissue constituents (i.e., cellulose, hemicellulose) decrease while breakdown products (i.e., bitumens, humates) increase. Humates predominate in highly decomposed peat. They are polymers of phenolic compounds, and commonly occur as humic acids or water-soluble fulvic acids. These two groups are of particular interest from a chemical perspective since they have a high absorptive capacity for metals and hydrocarbons (Pheeney and Radforth, 1972; Kerndorff and Schnitzer, 1980; see Section 5.2.1).

More detailed discussions of the organic chemistry of peat are presented in Clausen and Brooks (1980), Fuchsman (1980) and, Washburn and Gillis (1982).

5.2 Acidity

5.2.1 pH and Cation Exchange Capacity

The acidity of the system appears to be controlled through a combination of pH, the weak acid buffering system (e.g., H_2CO_3 - HCO_3^-; HFA-FA^-) and cation exchange reactions. These interrelated properties, directly or indirectly control both bioavailability and discharge concentrations of nutrients or toxins and peat accumulation rates (through regulation of microbial and fungal activity).

pH is often used to differentiate between ombrotrophic and minerotrophic systems. These two designations are based on the concept that waters of different origins have different concentrations of H^+ ions. Ombrotrophic systems contain high concentrations of H^+ and therefore exhibit low pH. Typical pH's of Sphagnum bogs range from 3.6-4.4 (Table 17). H^+ ions are derived from several sources. Clymo (1963, 1967) contends that most are introduced through cation exchange with both living plants and peat, while

TABLE 16a: ELEMENTAL COMPOSITION OF THE ORGANIC MATTER IN PEAT. (Monenco, 1981)

	C%	H%	0%	N%	S%
H1-2	48-53	5.0-6.1	40-46	0.5-1.0	0.1-0.2
H5-6	56-58	5.5-6.1	34.39	0.8-1.1	0.1-0.3
H9-10	59-63	5.5-7.0	31.34	0.9-1.9	0.2-0.5

TABLE 16b: AVERAGE PERCENTAGES OF VARIOUS ORGANIC MATTER IN PEATS OF VARYING DEGREE OF HUMIFICATION (after Assarsson, 1961 as cited in Monenco, 1981)

	H1-2 % Dry Matter	H5-6 % Dry Matter	H9-10 % Dry Matter
Cellulose	15-20	5-15	-
Hemicellulose	15-20	10-25	0-1
Lignin	5-40	5-30	5-20
Humates	0-5	20-30	50-60
Bitumen	1-10	5-15	5-20
Nitrogen compounds (similar to protein)	3-14	5-20	5-25

TABLE 17: CHEMICAL ANALYSES OF PEAT (Total concentrations in peat)

Location	Peat/ Peatland (no. of sites)	Depth (cm)	pH	Total N mg/g	TP mg/g	K mg/g	Ca mg/g	Mg mg/g	Na mg/g	Fe mg/g	Al ug/g	Mn ug/g	Cu ug/g	Pb ug/g	Zn ug/g	Hg ug/g	As ug/g
Newfoundland (Pollett, 1972)	bog (706)	0	3.5	6.7	0.34	0.37	1.24	1.17		0.74		45-67			0.030		
		-30	-3.8	-8.4	-0.41	-0.58	-3.09	-2.21		-0.92					-0.031		
	fen (226)		4.2	13.8	0.54	0.37	5.07	1.31		2.09		94-295			0.026		
			-6.5	-20.9	-1.03	-1.01	-30.63	-3.21		-10.07					-0.078		
New Brunswick, Kent County - (New Brunswick DNR, 1983)	open bog	20		5.5	0.05		370		0.1	0.5		256	1	17	56		
		-360		8.0	-0.3		-6380		-1.2	-75.0		-14	-15	-0	-8		
northern New Brunswick	cupiferous bog											4,320	$5.6x10^4$	34	2	0.32	5
southern New Brunswick (Boyle, 1977)	cupiferous bog											2,275	$2.8x10^4$	73	196	0.19	8
southwestern Nova Scotia (Nova Scotia Dept. Mines, 1983)	bog (2)					1.24-1.55	4.57-9.04	3.8-6.2	1.58-2.09	2.11-3.65	5.72-8.22	310-700	102-121	62-76	380-605		
Quebec, (Lavesque et al., 1980)	Swamp (5)	0-150			0.1		5.3-15.0	0.65-3.30		0.7-1.5	450-787	3.7	3.7	1.7	6.7		
												-120.0	-6.5	-8.0	-16.0		
northern Ontario Galbraith Twp.	Bog	0			-0.2	0.7	?	-2.8	-1.0	0.4	?	4-90	3-13	5-36	2.5	20-40	0.2
		-310					-1.1			-2.9	-2,800				-43.0		-1.2
Timmins area	Bog	0								0.5		5-37	4-5	5-28	3.0		0.6
		-350								-2.0					-46.0		-1.4
James Bay Lowlands (Shotyk & Telford, 1983)	Bog-Fen	0								0.3		4-32	1-9	4-22	2.0		0.2
		-350								-2.0					-25.0		-2.1
northern Ontario	Fen	0	6.2	0.7	0.2	0.1	0.3	0.5		1.1	676	33	4-12	2-25	6-58	0.01	1
		-290	-6.6	-2.8%	-0.7	-1.4	-2.6%	-1.3		-5.8	-1341	-1209				-0.12	
Hearst area	Bog	0		0.8	0.2	0.1	0.3	0.2		0.4	738	4	3-5	2-28	3-32	0.01	1
		-245		-1.7%	-0.4	-1.0	-1.7%	-0.6		-1.7	-1649	-37					
Ontario clay belt (Stanek et al., 1977)	Swamp (38)	0-50		12.12	0.69	3.69	19.34										
	Fen (11)			18.35	0.84	2.91	11.08										
	Bog (28)			11.87	0.54	1.18	4.37										

TABLE 17: CHEMICAL ANALYSES OF PEAT (Total concentrations in peat) (cont'd)

Location	Peat/ Peatland (no. of sites)	Depth (cm)	pH	Total N mg/g	TP mg/g	K mg/g	Ca mg/g	Mg mg/g	Na mg/g	Fe mg/g	Al ug/g	Mn ug/g	Cu ug/g	Pb ug/g	Zn ug/g	Hg ug/g	As ug/g
northern Ontario (Glooshenko and Capobianco, 1982)	Bog (19)	0-40												7	25	56	0.01 -0.11
	Fen (23)	0-40												13	29	58	
	Swamp (8)	0-40												16	27	62	
south Germany (Waughman and Bellamy, 1976)	extreme rich fen (6)	0-15	7.1	12													
	rich fen (6)		6.8	14													
	intermediate fen (6)		6.1	15													
	poor fen (9)		5.0	18													
	extreme poor fens (6)		4.3	14													
	bog (17)		3.8	12													
southern Sweden (Damman, 1978)	Bog	0-400				0.02-0.18	0.4-1.7		0.12-0.6	0.2-3.5							
south Finland (Pakarinen and Tolonen, 1976b)	Bog (7)	40								0.4-1.2		70-114	10.6-14.3	56-78	190-218		
northwest to central west Finland (Pakarinen and Tolonen, 1976a)	Bog (15)	3.5								0.1-0.4		32-253	3.8 -22.2	2.5 -9.1	24-48	0.010 -0.085	
Ireland (Shotyk & Telford, 1983)										5-1		17-	2	4	3.5		0.3

Hemond (1980), utilizing a mass balance approach, argues that the effect of cation exchange is relatively small, and that the low pH of bogs is maintained by dissociation of weak organic acids produced in plant decomposition. The anaerobic production of H_2S and subsequent oxidation to H_2SO_4 contributes smaller amounts of H^+ (Gorham, 1956). In areas which are not affected by industrial pollution, H^+ input through precipitation is less than 30%. However, acid precipitation can contribute significant quantities of H^+ (Likens et al., 1977).

In minerotrophic systems the relative contribution of H^+ to total ionic composition is decreased by the input of large quantities of Ca^{2+}, Mg^{2+}, carbonate and other ions carried by mineral-rich groundwater (Moore and Bellamy, 1974). This results in pH's which typically range between 4.5-8.0 (Table 17).

Cation exchange reactions regulate the composition and concentrations of soluble cations. In the exchange process some ions are removed from solution and adsorbed to the peat particle, while others are released. The number of sites potentially available for cation exchange is determined by the particle surface area. Peat has an extremely large surface area, exceeding even that of montmorillonite clay by 2-4 times (Brady, 1974). Sphagnum peat, with its high permeability and large pore spaces has a higher cation exchange capacity than sedge peat. Puustjarvi (1977) reports typical values (at pH7) of 100-160 meq/100g for Sphagnum peat and 40-100 meq/100 g for sedge peats. However, the amount of exchange occurring at a given time is governed by the electrovalent charge imbalance between the peat particle and the solution, which is in turn pH-dependent. The peat particle may be characterized as a complex organic colloid consisting of a central unit; composed primarily of carbon, hydrogen and oxygen, (humates) with associated carboxyl and hydroxyl groups. These impart a net negative charge to the particle. At the low pH typically encountered in ombrotrophic bogs, greater than 90% of the exchange sites are occupied by H^+ ions. Consequently the negative charge is weak, and cation exchange is low. In minerotrophic systems the input of Ca, Mg and other mineral-derived cations increase the solution pH. This causes the bound H^+ to ionize and allows replacement by other cations.

The kinetics of ion exchange is related to the simultaneous action of two opposing effects, both of which are dependent on cation concentration (Bunzl, 1974; Bunzl et al., 1976). In the initial phase of the reaction, the rate of exchange progressively increases as

cation concentrations increase. However, as exchange sites on the peat become more saturated, the rate of exchange decreases. The kinetics of exchange (particularly kinetics of release) is an area critical for chemical transport modelling, which has received little attention to date.

Cation adsorption is selective. Trivalent cations are sorbed in favour of divalent ions, and divalent in favour of monovalent (Sikora and Keeney, 1983). Laboratory studies show that adsorption of major ions by organic acids (i.e., humic and fulvic acids) derived from peat follows the general order of:

$$H > Ca > Mg > K$$

Numerous studies have also documented trace metal chelation with organic soils (i.e., Rashid, 1974; Kendorff and Schnitzer, 1980). However, caution must be exercised when applying these results to whole peats since most are based on complexation by weak organic acids (humic and fulvic acids) extracted from the peat. Davies et al. (1969) note that retention of copper by sedge peat is greater than by the humic acid extract. The general order of sorption strength at pH 4.7 is:

$$Hg = Fe = Pb = Cu = Al = Cr > Cd > Ni = Zn > Co > Ca > Mn$$

Minor variations in this sequence occur in response to pH, and initial metal concentrations (Rashid, 1974; Kerndorff and Schnitzer, 1980).

5.2.2 Buffering Capacity

The capacity of peatlands to resist changes in pH has been the subject of considerable debate with respect to effects of acid precipitation and downstream impacts of acid drainage water upon aquatic communities. The debate appears, in part, to result from a lack of understanding of the factors which regulate acidity (described in the previous section). The following discussion describes buffering mechanisms and potential impacts of acid rain, as currently understood. It should, however, be emphasized that this area requires further study, including re-evaluation of much of the acid rain data collected from boreal and temperate regions of Canada.

Unlike mineral soils, in which buffering capacity is determined largely by the concentration of carbonates, the buffering capacity of peat is determined by its ability to remove H^+ ions from solution through cation exchange, and dissociation constants of weak organic acids. Since the cation exchange capacity of peat is greater than mineral soils, a high buffering capacity is expected. However, early experiments by Wilson and Plice (1933) showed that the buffering capacity of dried peat could be directly related to pH; soils with higher pH (>6) were significantly more resistant to depressions in pH caused by addition of hydrochloric acid, than low pH soils. Thus, the buffering capacity of minerotrophic peatlands appears to be directly related to the concentrations of exchangeable cations such as Ca and Mg, and of anions such as carbonate, whereas in ombrotrophic peatlands, in which reducing conditions prevail, acidity is controlled by dissociation constants (Pk) of organic acids. Since these are weak acids, their large reservoir of hydrogen ions regulates and buffers the pH.

Hemond (1980) showed that in an ombrotrophic bog in Massachusetts, large inputs of mineral acidity through acid rain were counterbalanced by biological reduction of sulphates and plant uptake of nitrates. Bayley (1984, pers. comm.) observed the same phenomenon in a bog in northwestern Ontario to which regular applications of H_2SO_4 and HNO_3 were made. Concentrations of sulphate stabilized at pre-spray levels within one week of application, while nitrate was totally removed within one day. Alterations in pH were minimal. Other authors have also noted the resistance of organically-dominated systems to decreases in pH (Fortescue et al., 1984). Hemond (1980) notes that large increases in sulphur input could significantly increase the rate of peat oxidation and lead to accumulations of toxic concentrations of hydrogen sulphide. However, Bayley observed little H_2S production in her ombrotrophic system, although detectable concentrations were recorded in a minerotrophic area.

In ombrotrophic bogs dominated by oxidation reactions, sulphuric acid, as opposed to organic acid, may be the main source of H^+ (Gorham, 1967). Coastal systems may be particularly influenced by sulphate from sea spray. The potential impact of acid precipitation on systems such as these has not been studied. However, it is likely that buffering capacity would be lower than in an organic acid-dominated system.

5.3 Nutrients

5.3.1 Nitrogen

Nitrogen occurs in three forms in peat:

- o organic nitrogen,
- o ammonia (as NH_4^+), and
- o nitrate compounds (NO_2^-, NO_3^-).

Approximately 95-98% of the total nitrogen in the system is contained in insoluble organic compounds associated with living plants, peat and microorganisms. This leaves only 2-5% of the total nitrogen in bioavailable inorganic forms (Brady, 1974; Richardson et al., 1978; Waughman, 1980). The cycling of nitrogen from organic matter to inorganic solutes which are subsequently reincorporated into organic form is tightly controlled by a complicated series of biologically-mediated chemical reactions (Figure 6). The relative amounts and ionic form of soluble nitrogen have direct bearing on primary productivity and nutrient yields. Nitrogen enters the system through ground and surface water inflow, precipitation, dry deposition and atmospheric fixation.

There is a trend of increasing total nitrogen concentration in peat along the bog-fen gradient, although considerable overlap exists between peatland types. These are likely the result of differences in precipitation chemistry. Typical nitrogen ranges in Canadian peatlands are similar to values reported from the United States and Europe (Table 17). Damman (1978) found that total nitrogen concentrations were relatively constant throughout peat profiles from coastal and inland bogs in Sweden (Figure 8).

Ammonia, in the form of NH_4^+, is the first bioavailable product produced from organic nitrogen decomposition. Further bio-oxidation produces nitrates (NO_2^- + NO_3^-) (Hall, 1982). This process, known as nitrification, involves two steps:

$$2NH_4^+ + 3O_2 \longrightarrow 2NO_2^- + 2H_2O + 4H^+ + \text{energy}$$
$$2NO_2^- + O_2 \longrightarrow 2NO_3^- + \text{energy}$$

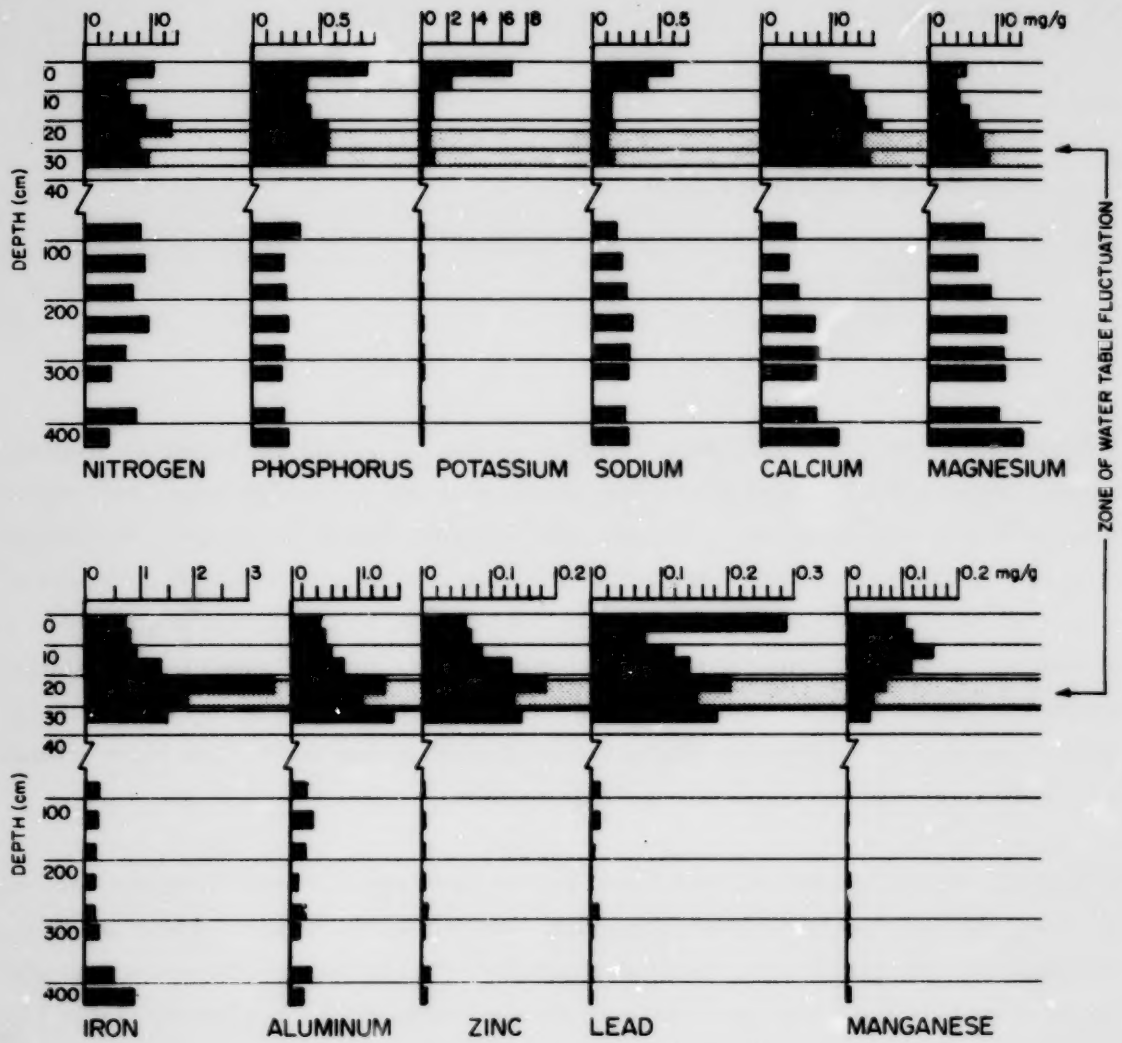


FIGURE 8
Distribution of Elements with Depth in Sphagnum Peat (After Damman, 1978)

These reactions normally occur in quick succession, but when NH_4^+ concentrations are extremely high, the second step may be delayed. Under anaerobic conditions, biochemical nitrate reduction occurs. This denitrification process may ultimately result in nitrogen loss from the peatland to the atmosphere:

$2HNO_3^- \xrightarrow{-2O_2}$	$2HNO_2^- \xrightarrow{-2O_2}$	$N_2O \xrightarrow{-2O_2}$	$N_2 \longrightarrow$	$2NO$
Nitrates	Nitrates $-H_2O$	Nitrous Oxide	Elemental Nitrogen	Nitric Oxide

Both nitrification and denitrification reactions occur in peatlands. The relative importance of each process is governed by the moisture-aeration gradient, redox potential, temperature, and rate of biotic uptake (Avnimelech, 1971). NH_4^+-N is the most important source of inorganic-N in all peatland types. However, concentrations are significantly higher in bogs than in fens (Richardson et al., 1978; Waughman, 1980). This is attributed to:

- the acid tolerance of ammonifying bacteria and the inhibition of nitrifying bacteria at pH's of less than 5 (Harmsen and Kolenbrander, 1965), and
- a chemical equilibrium which favours NH_4^+-N over NO_2^-N and NO_3^-N at low pH and redox potential (Campbell, 1970).
- anaerobic conditions and hydrologic regimes in bogs which minimize the oxidation of ammonia and its transport out of the bog.

Typical concentrations of nitrates are 100-1,000 times less than NH_4-N. Literature values for nitrates are often reported as NO_3^-N; however, Waughman (1980) found no detectable NO_3^-N in south German peats. These values should, therefore, be interpreted as NO_2^- + NO_3^-N. Similar results have been reported from other locations. Engler et al. (1976) showed that NO_3^- is rapidly removed from ground or surface water overlying water-logged soils, even when oxygen is present. They concluded that as NO_3^- diffuses into the anaerobic layer, it is rapidly reduced through bacterial respiration. Richardson et al. (1978) report seasonal and depth-related variations in inorganic nitrogen concentrations at Houghton Lake Fen, Michigan, which are related to hydrological regime, microbial uptake and peat exchange characteristics.

5.3.2 Phosphorus

Native phosphorus is supplied to soil systems through weathering or erosion of apatite minerals. Precipitation is not a significant source of phosphorus. Consequently, total phosphorus concentrations in peatlands are low relative to mineral soils. Typical concentrations in peat range from 0.5-1.00 mg/g. Characteristic increases along the bog-fen-swamp gradient reflect the increasing influence of mineral-enriched waters (Table 17).

Because of these low concentrations, phosphorus has traditionally been considered a growth-limiting element, especially in ombrotrophic systems. However, phosphorus extraction studies show that the relative percentage of bioavailable-P in bogs is generally higher than in fens and may be several orders of magnitude greater than in mineral soils (Malmer, 1962; Saebo, 1969; Richardson et al., 1978; Waughman, 1980). This suggests that the nutrient deficiency problem may be related to uptake rather than supply. This observation contradicts the bulk of the literature. However, the majority of peatland-related studies have been concerned with characterizing total phosphorus concentrations rather than total dissolved phosphorus or bioavailable phosphorus concentrations.

Phosphorus bioavailability is largely determined by pH and interrelated factors such as moisture-aeration regime, soluble Fe, Al and Mn, available Ca, peat humification and microbial activity. In a typical Sphagnum peat profile, most of the phosphorus in the aerated surface peat is in organic form, sorbed to the peat, or complexed with humic and fulvic acids (Stanlick, 1976). Below this level, or when reducing conditions prevail, solubilization occurs. Between pH 4-7, $H_2PO_4^-$ is the dominant ionic form. It is considered to be readily bioavailable. However, if Fe, Al, Ca or Mn ions are also present, they will quickly react with the phosphate ion to form insoluble compounds which are unavailable for plant uptake (Brady, 1974; Damman, 1978).

5.4 Major Cations

Calcium, magnesium, potassium and sodium exhibit similar chemical behaviour in peatlands. All are required by plants, and are important in the ion exchange complex.

Concentrations of calcium and magnesium in peat and peat water are often used to differentiate between ombrotrophic and minerotrophic conditions since they are largely supplied through solution of carbonitic minerals and subsequent transport by mineral-rich groundwaters. Of the two, calcium is usually dominant, although high concentrations of Mg occur in coastal peatlands as a result of sea-salt influences on precipitation (Sonesson, 1970).

There is evidence that K may limit phytoproductivity under certain conditions, while Na is generally supplied in larger quantities than required (Damman, 1978). Total K concentrations in peat are on the order of 10% of the concentration in mineral soils. A trend of increasing concentration is often observed between ombrotrophic and minerotrophic peats. However, high within-site variations occur and considerable overlaps between peatland types have been reported (Table 17). These discrepancies are attributed to differences in precipitation chemistry and seasonal distribution (Verry, 1975). Gradients in Na concentrations are similarly correlated to precipitation chemistry. Concentrations generally decrease with distance from the coast (Damman, 1978).

These major cations are highly exchangeable in peatlands. Brady (1974) reports that 75 to 80% of the total Ca, 51 to 100% of total Mg and 27 to 34% of total K are exchangeable in organic soils. This compares to 35%, 10% and less than 1%, respectively, for mineral soils. The relative percentage of exchangeable Ca + Mg appears to be higher in bogs than fens, although absolute concentrations are less.

The major cations exhibit distribution patterns in peat profiles, characterized by surface accumulations and rapid decomposition with depth (Figure 8). Potassium is actively taken up by living vegetation, while uptake of other elements is thought to occur through cation exchange. Upon decomposition, the cations are released from the organic complex and become available for exchange or are leached from the system. Tyler (1972) and Damman (1978) observed a reverse trend to the one described above for Mg concentrations in peat (Figure 8). This may be the result of variable inputs, total ionic composition, exchange chemistry of the peat or influence of mineral parent material.

5.5 Trace Elements

The composition and concentration of trace elements in peat is highly variable (Table 17). Atmospheric fallout and bedrock geology are major sources of trace metals input. The ability of the peatland to retain or release metals is related to vegetation type, hydrological characteristics, moisture-aeration regime, peat depth and decomposition. Most of the metals listed above exhibit similar chemical behaviour in peatlands. Distributions within the profile are largely related to pH and redox potential. Concentrations are typically high in the surface aerated zone, decrease rapidly in the waterlogged anaerobic layers, and increase at the mineral-peat interface (Figure 8; Damman, 1978).

Observed surface accumulations of trace metals such as Cu, Pb, Zn, Hg and As are largely due to atmospheric pollution (numerous citations in Washburn and Gillis, 1982; Arafat and Glooschenko, 1982; Percy, 1983). These elements typically exhibit higher surface concentrations in bogs than in fens (Waughman, 1980). Livett et al. (1979) showed that concentrations of the first three elements in surface peat layers of a British blanket bog are significantly correlated to the size of the nearest urban centre. Glooschenko (1984, pers. comm.) traced elevated concentrations of metals in bog plants at distances of up to 250 km downwind of the Sudbury, Ontario, "super-stack". Typical concentrations in remote peatlands are generally low, and exhibit little variation between peatland types (Pakarinen and Tolonen, 1976; Glooschenko and Capobianco, 1982). However, in mineral-enriched areas, high concentrations of trace elements may occur throughout the entire profile (i.e., Boyle, 1977).

Concentrations of Fe, Al and Mn are typically higher in fens peats (Waughman, 1980). These elements are present in relatively low concentrations in precipitation, and are assumed to be derived primarily from enriched groundwater.

Under aerobic conditions, metals, present as inorganic ions and compounds, are complexed with humates, sorbed onto peat solids or are present as insoluble oxides (i.e., MnO_2) partially hydrated hydroxides (Fe-OOH)or minerals derived from the incongruent dissolution of parent soils and bedrock. However, under anaerobic conditions, reduction occurs and the metal can be solubilized. The ease of solubilization is related to pH, and generally follows a trend of Fe, Al, > Zn, Mn, Cu > Pb (Damman, 1978). Soluble metal

compounds are quickly lost from the system through leaching. If sufficient aqueous sulphide is present, trace metals may rapidly re-precipitate as metal sulphides. The exact mineral species which form are difficult to predict due to the potential number of oxidation states of sulphur. It is interesting to note that Pb may be susceptible to solubilization, since this metal is often used to date peat deposits (Damman, 1978; Livett et al., 1979; Hemond, 1980). Solubilization would result in underestimation of decomposition rates. Whether Pb is present in peat in the inorganic form in which it originally entered the peat bog from the atmosphere, as an insoluble sulphide (in anaerobic conditions), or as an organic solid form is not known. Recent work in lake sediments suggests that Pb-210 may be present mainly in the organic form (Evans, pers. comm.).

Trace organic contaminants have also been observed to accumulate in peatlands. Rappaport (1984, pers. comm.) notes that the half-life of metabolic derivatives of DDT may range up to 100 years under aerobic conditions, but is considerably shorter under anaerobic conditions. PCB's appear to be lost from peatland systems much more rapidly than DDT and its derivatives.

6.0 WATER CHEMISTRY

The chemical characteristics of peatland discharge waters and their rate of flow influence the composition and quality of aquatic communities. To date, this area of peatland ecology has been largely neglected (see Section 7.0). However, "brown water" lakes, rivers and streams have been locally identified as habitats of economically important fish species (Clarke-Whistler and Rowsell, 1983). Perhaps because the aquatic ecology of peatlands is so poorly understood, much controversy has centred around the type and magnitude of aquatic impacts arising from large-scale peat mining. These arguments are largely based on extrapolations from non-peatland areas. However, basic differences in ecological factors which control the chemistry of organically-dominated and mineral systems suggest that, for some parameters such as pH, direct comparisons may be invalid. It is, therefore, essential that the complete chemistry of peatland waters be characterized.

As discussed in previous sections, peat water chemistry is the result of complex physico-chemical and biological interactions between vegetation, peat, inflow waters and precipitation. There exist characteristic chemical differences between waters from bogs, fens or swamps. These are summarized in Figure 9. As expected, concentrations of major cations (Ca, Mg) and total ions (conductivity) are greater in fen waters, while concentrations of organically-derived nutrients, acidity and soluble metals (i.e., Fe, Al) are typically higher in bog waters (Verry, 1975; Schwintzer and Tomberlein, 1982; Clausen and Brooks, 1983).Factor analysis of 22 physico-chemical parameters from shallow peat waters of Michigan peatlands produced the following major groupings (Schwintzer and Tomberlein, 1982):

Factor I:	Ca, Mg, Si, pH, alkalinity, conductivity, (Na)
Factor II:	bioavailable - P, total P, NH_4^+, K
Factor III:	Na, (Cl), (K)

These three factors explained more than 80% of the total variation observed in vegetational composition. Peatland types were classified on the basis of factor loadings. The authors interpreted Factor I as a reflection of telluric influence, and II to explain differences in the state of decomposition of organic matter. Bogs rated low for I and intermediate for II and III. Fens and swamps were high for I, and fens rated lower for

Figure 9

Characteristic Differences in the Water Chemistry of Bogs and Fens

	Acidity	
	Bog	Fen
pH	↓	↑
Electrical Conductivity	↓	↑
Alkalinity	↓	↑
Total Phosphorus	↓	↑
Total Nitrogen	↓	↑
Ammonia	↓	↑
NO_3 & NO_2	↓	↑
Potassium	=	=
Calcium, Magnesium	↓	↑
Iron	↑	↓
Aluminum	↑	↓
Sodium	↓	↑
Oxygen	↓	↑

TABLE 18: PEATLAND WATER CHEMISTRY (all concentrations in mg/L unless otherwise noted)

Location	Peatland Type	pH	Alkalinity $CaCO_3$	Elect. Cond. umhos/cm (25°C)	Suspended Solids	Total N	NH_4	NO_3	P	K	Ca	Mg	Fe	Al	Mn	Cu	Pb	Zn ug/L	Hg ug/L	As
Quebec (B. Coupal, pers. comm., 1982, as cited by Washburn and Gillis, 1982)	Bog	3.9-4.2		20-29			0.02				932-1.6									
Marcell Res. Stn. Minnesota (Verry, 1975)	Bog (14-172)	3.6	0	51		1.34	0.45	0.20	0.19	1.3	2.4	0.97	1.35	0.79	0.06	0.04	0.05	0.08		
	Fen (3-22)	6.5	54	125		0.58	0.15	0.10	0.09	1.1	16.6	2.88	0.98	0.16	0.08	0.18	0.05	0.11		
Marcell Res. Stn., Minnesota (Verry, 1975) - flow weighted concentrations	Bog				1.1			0.05	0.8	2.0	0.9	1.0	0.60	0.05			0.05			
	Fen				2.6			0.03	1.1	16.6	2.9	1.0	0.16	0.09			0.11			
northeast Minnesota (Clausen, 1980)	Bog (30)	5.5		33	9.0	1.0	0.		0.07		4.92	1.55	1.90	0.38	0.07				9.2	2.3
	Fen (34)	6.7		104	23.0	1.4			0.07		17.53	5.38	2.41	0.30	0.02				5.5	3.2
northern Michigan (Schwintzer and Tomberlein, 1982)	Bog (6)	4.0	0	57			0.45	0.08	0.16	0.7	2.3	0.5								
	Fen (6)	6.5	153	262			0.18	0.006	0.03	0.5	44.5	10.5								
	Swamp (15)	6.9	213	405			0.62	0.005	0.2	0.9	59.8	14.2								
South-Central Finland (Tolonen, et al.,1979.)	Bog (9)	3.6-4.3		5.6		1.5	0.2		0.15	1.29	0.11-3.12	0.10-0.98	2.98	0.26	1.00	0.01	0.13	0.04	2.6	
	Fen (6)	4.1-4.4		12-16		1.2	0.1		0.04	0.75	0.85-1.49	0.05-0.60	0.40	0.08	0.11	0.01	0.13	0.04	2.4	
northern Minnesota Brooks et al., 1982)	Bog (66)	5.6	10.1	45	5.1	1.5	0.1	0.06	0.06	1.24	6.76	2.37	2.64	0.55	0.14				6	
	Fen (56)	7.0	76.5	171	5.4	1.8	0.2	0.08	0.08	1.15	27.27	7.90	2.37	0.25	0.29				5	

Factor II than swamps. These results were corroborated in studies of Minnesota peatlands, where Brooks et al. (1982) found statistically significant correlations between a number of chemical parameters, sampled on a seasonal basis. Analysis of the study results, displayed in Figure 10, reveal three major groupings of parameters.

Group I represents groundwater influence and Group 2 contains organically-derived nutrients. The two groups are linked through a third group which represents a combination of acidity and oxygen-reduction potential. Diagnostic parameters included in this group are:

- o acidity
- o dissolved oxygen
- o iron and aluminum
- o chemical oxygen demand (COD).
- o pH
- o colour

The results of these two multivariable studies are supported by numerous European investigations (i.e., Sjors, 1950; Gorham, 1956; Tolonen et al., 1979). To date, no comparable Canadian studies have been published, however, similar results would be expected.

Comparisons of reported concentrations of water quality parameters from North American and European peatlands show strong variations in many parameters (Table 18). These are related to differences in peat accumulation rates, outflow velocities, seasonal effects, ion exchange characteristics of the peat, anthropogenic inputs, and precipitation chemistry and distribution (Sparling, 1966; Pakarinen and Tolonen, 1976a; Hemond, 1980; Brooks et al., 1982).

Sparling (1966) and Verry (1975) found that concentrations of many constituents of bog discharge exhibit negative correlations with streamflow rate. These include:

- o total-N, total-P, colour, conductivity, Ca, Mg, Fe, Al, Na, Mn, Zn.

Seasonal variations in hydrological regime may temporarily alter this relationship. For example, total phosphorus concentrations have been shown to increase by up to 350% during snowmelt relative to average annual concentrations (Saebo, 1969).

Potassium and dissolved oxygen concentrations are positively correlated with flow rate. In the case of potassium, this is likely due to increased leaching as a result of high precipitation input and/or flow, while increased oxygen concentrations result from improved atmospheric reaeration. Sparling (1966) also found an increase in pH with water movement, which he attributed to cation exchange of H^+ ions; however, Verry (1975) did not observe this. It is also interesting to note that Brooks et al. (1982) found no significant correlations with discharge rates for any water quality parameters.

No comparable correlation between streamflow rate and water quality parameters is observed in fens. In these systems, the base flow and more regular discharge may mask such effects (Verry, 1975).

Few estimates of annual yields of nutrients and trace elements have been attempted (Table 19). Potentially large errors are associated with all of the reported results. In particular, the direct influence of minerotrophic systems on outflow is difficult to assess since the groundwater drainage area cannot be accurately calculated. Verry (1975) concluded that nutrient yields from treed bogs were similar to yields from upland forests in the humid boreal region of North America. He also concluded that total yields of organically derived nutrients from bogs and fens was similar if bog water concentrations were flow-weighted to reflect the inverse relationship between concentration and flow rate. However, peatlands comprised less than one-third of Verry's total study area. Nutrient yields from an undisturbed blanket bog in Ireland were up seven to ten times greater than the Minnesota values for nitrogen and calcium, and two to four times greater for phosphorus and potassium (Burke, 1975). Total yields from an eroding bog in England were higher still although particulates accounted for the bulk of the yield (Crisp, 1966).

TABLE 19: NUTRIENT YIELDS FROM PEATLAND ECOSYSTEMS

Location	Peatland Type		Nutrients (kg/ha/yr) N	P	K	Ca	Mg	Pb
Minnesota (Verry, 1975)	treed bogs		1.91-1.97	0.08	1.26-1.41	3.46-3.55		
Ireland (Burke, 1975)	open bog		11.2*	0.15	4.7	22.0		
England (Crisp, 1966)	eroding blanket bog	(dissolved)	2.94	0.39	8.97	53.81		
		(total)	17.68	0.86	11.05	58.66		
Massachusetts (Hemond, 1980)	open bog		-	-	1.10	-	0.72	0.01

* NO_3-N + NH_4-N

7.0 AQUATIC COMMUNITIES OF UNDISTURBED SYSTEMS

The protection of aquatic ecosystems is a major consideration in the development of peatlands. Aquatic communities typically include mammals, birds, fish, reptiles and amphibians, the plants and organisms on which they feed, and the physical-chemical environment in which they live (Clarke-Whistler and Rowsell, 1983).

The potential zone of influence of peatland drainage extends from the surface waters in the peatland itself, to the lake or sea into which the watershed ultimately empties. In general, peatland runoff exerts a diminishing influence with increasing distance downstream, due to dilution, dispersion and transformation of substances in the peat water. Peatland watersheds may include small brooks and large rivers, as well as small ponds and large lakes. The relative importance of each type of environment is unique to each watershed, and depends on topography, climate and hydrologic processes.

Since peatlands are formed in locations where the rate of peat deposition exceeds the rate of removal by decomposition and weathering processes, they are often directly drained by small streams having little potential for erosion. Such streams typically join other streams to form progressively larger watercourses, with ponds and lakes occurring along the way. Factors affecting the development of biological communities in each habitat include the environmental requirements of each species (e.g., temperature, nutrient levels, oxygen levels, turbidity, pH, currents, etc.) and biotic variables (e.g., predation, availability of food, competition, etc.). Man's intervention in the ecosystem, either through removal of biotic components (eg., fish harvesting), or by changing the physico-chemistry of the water can effect profound changes in the structure of aquatic communities.

In constructing an impact assessment framework to evaluate peatland development, it is necessary to describe components of natural aquatic communities at a level which can be applied to different geographic areas having exploitable peat resources. Therefore, in this study, we characterize aquatic communities by physical habitat types and trophic levels.

7.1 Aquatic Communities within Peatlands

The aquatic communities of pools and local depressions located within a peatland which is scheduled for development will likely be eliminated; thus, some discussion of these communities is appropriate.

Bogs and fens with high rates of organic matter input are termed "dystrophic". Dystrophy implies that inputs of internally produced organic matter (allotrophic) exceed externally produced inputs (autotrophic) (Wetzel, 1975); thus, fens may be considered less dystrophic than bogs. Dystrophic waters are often referred to as "brown-water" systems, due to the brownish tea colouration of the water imparted by dissolved humic substances. Primary producers in dystrophic environments include macrophytes (e.g., Sphagnum, sedge) and phytoplankton. In bogs and fens, macrophytes dominate community productivity (Section 3.3). Dystrophic waters generally have low phytoplankton productivities, since the effects of poor light penetration and acidic conditions, (particularly in ombrotrophic bog waters) inhibit phytoplankton growth (Wetzel, 1975). Woelkerling (1976) studied the algal communities of several ombrotrophic and minerotrophic peatlands in Wisconsin. Desmids and blue-green algae were generally more prevalent in bogs, while diatoms were usually dominant in more alkaline peatlands. In Dutch moorland pools, numbers of both diatom and desmid species were found to decline as conditions became more acidic (Coesel et al., 1978; Van Dam et al., 1980). Phytoplankton productivities (NPP) are generally in the range of $<$ 50-500 mg C/m^2/day for dystrophic lakes.

The zooplankton of bog lakes is usually dominated by testaceous, rhizopod protozoans and rotifers (Wetzel, 1975; Foran and King, 1981). Crustacean zooplankton species are generally intolerant of acidic bog conditions, but may be more important in minerotrophic systems.

Data on benthic invertebrates in bog waters are relatively sparse. Based on acid rain studies, larval insects that rely on external body surfaces (e.g., gill structures) for respiration are rare in acidic conditions (Harvey et al., 1981). In contrast, air-breathing organisms such as adult coleopterans, larval culicids, hemipterans, etc. are more resistant to acidity. Molluscs, most of which require relatively hardwater conditions, are generally absent in acidic waters (e.g., Haines, 1981) and thus are not expected to be

important in ombrotrophic bog waters, but may be common in fens and swamps (Judd, 1966).

Nearly all fish species found in Canadian freshwaters occur in watersheds receiving peatland drainage; however, relatively few species occur in bog waters themselves. Central mudminnows (Umbra limi) are perhaps more tolerant of low pH than other freshwater species, and have been reported in acidic bog water at pH 4.0 in Wisconsin (Rahel and Magnusen, 1983). Yellow perch (Perca flavescens) may also be found in acid bog lakes (Rahel, 1983). Scott and Crossman (1973) note that finescale dace (Chrosomos neogaeus), northern redbelly dace (Chrosomos eos), pearl dace (Semotilus margarita), fathead minnow (Pimephales promelas) and brook stickleback (Culaea inconstens) typically occur in boggy or swampy habitats in Canada. Figure 11 shows the pH tolerances of fish species which occur in naturally acidic Wisconsin lakes (Rahel and Magnusen, 1983). These lakes were classified as seepage lakes (no surface water inflow) and drainage lakes (with surface water inflows). Many were brown water lakes in peatland areas and might be considered bog lakes. No salmonids were present, apparently due to high temperatures in summer and relatively low dissolved oxygen conditions. Among the fish species that may be present in bog waters, yellow perch is perhaps the most important in terms of its tolerance of acidic conditions, its widespread occurrence in Canada, and its economic importance as a commercial and game fish.

7.2 Downstream Aquatic Systems

7.2.1 River and Stream Ecosystems

Several important physical and chemical parameters control the composition of aquatic communities in streams and rivers. Aquatic species vary in their preferences for temperature, current, turbidity, substrate types, shoreline (edge) cover, and water chemistry. The volume of water discharged in a watershed increases with distance downstream. Headwater tributaries have narrow channels, and are often more shaded by trees and shoreline vegetation than large streams or rivers further downstream. Water velocities are generally reduced in larger streams than in their headwaters, due to generally decreasing gradients with distance downstream. Thus, erosive forces are important in headwaters, while deposition of eroded materials occurs in the slower-flowing lower river. The lower river is also typically more turbid, due to inputs of

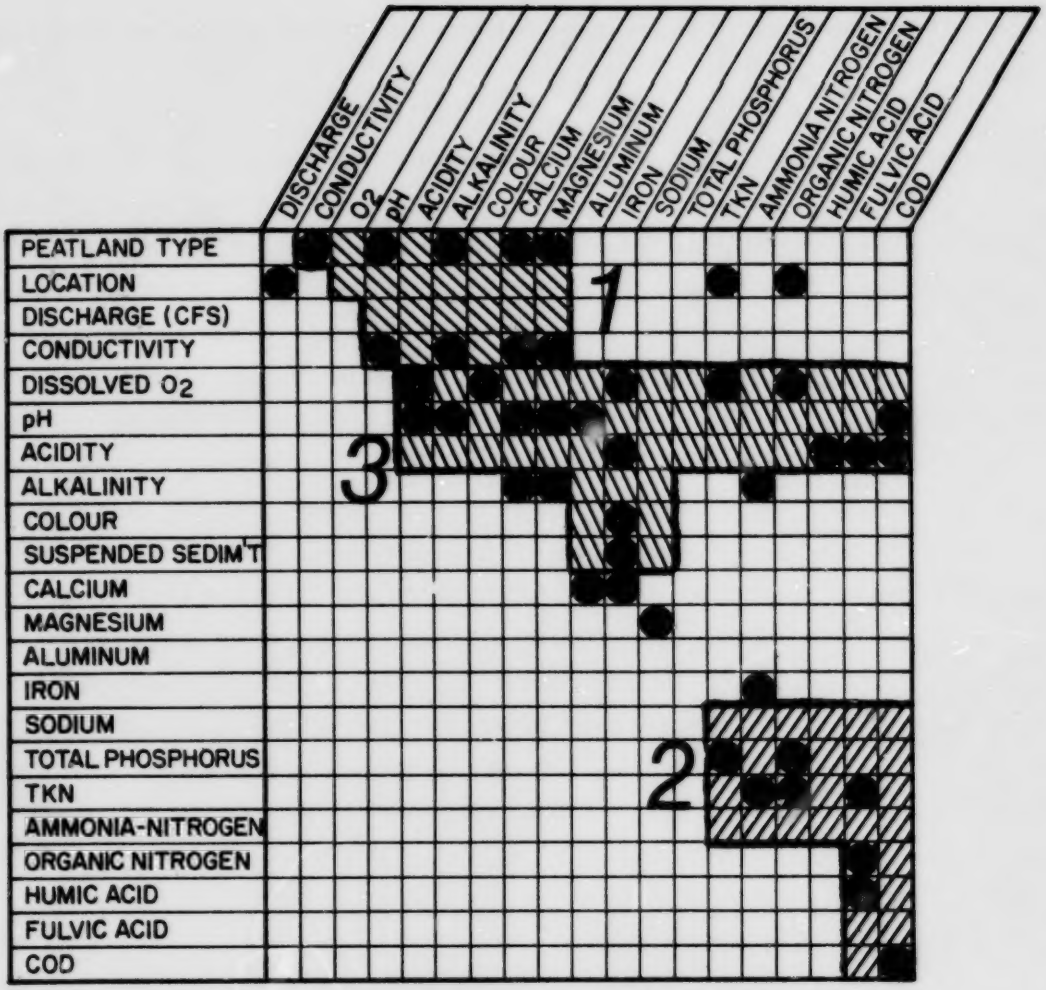


Figure 10

Minnesota Peatland Water Chemistry Parameters which were Significantly Correlated ($p<.05$) (Modified from Brooks et al,1982)

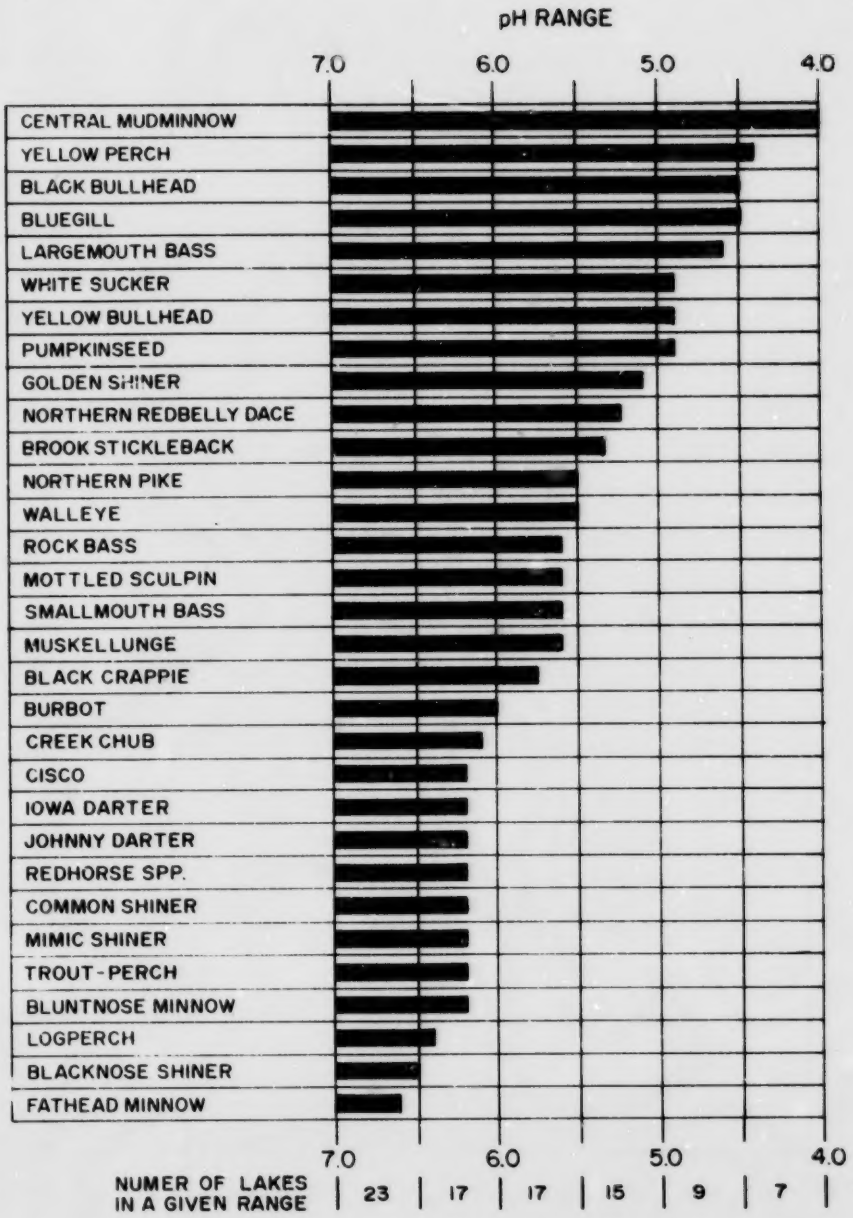


Figure 11

Distribution of 31 Fish Species in Relation to pH for 138 Northern Wisconsin Lakes

From Rahel and Magnuson, 1983

suspended sediments from the tributaries. In headwaters, water temperatures remain relatively low due to shading, and flowing conditions help maintain high dissolved oxygen levels. Larger rivers are more open to insolation. Higher temperatures in combination with reduced flow conditions may lead to fluctuating dissolved oxygen levels.

Peatlands provide sources of dissolved and particulate organic carbon to downstream aquatic systems. Communities of rivers and streams rely on allochthonous and autochthonous organic matter in their total energy metabolism. The relative roles of various carbon sources in driving the metabolism of stream ecosystems is dynamic and depends on locally and seasonally variable environmental conditions (Wetzel, 1975). In heavily shaded woodland streams, community respiration may often exceed the rate of primary productivity (De La Cruz and Post, 1977). These systems rely on materials, supplied through litterfall, litterblow, throughfall and subsurface drainage to meet their energy requirements (Fisher and Likens, 1973). Generally, as stream size increases, so does the relative importance of autochthonous organic matter in community metabolism due to increasing rates of photosynthesis and the declining importance of allochthonous sources.

The processing of dissolved organic carbon (DOC) is accomplished primarily by benthic and planktonic bacteria (Cummins et al., 1972). Benthic invertebrates break down particulate organic carbon (POC) into finer particles, thereby catalyzing further bacterial breakdown (Hynes, 1970). Microflora provide the food base for larger consumer organisms. A simplified compartmental model for organic matter in streams is shown in Figure 12. In this figure, "upstream organic matter" includes organic matter exported from peatlands.

The important primary producers include attached algae (periphyton or aufwuchs) and rooted aquatic macrophytes. As outlined above, their importance in stream metabolism may be overshadowed by allochthonous organic matter, particularly in small headwater streams. The periphyton of streams is highly dependent upon substrate type and water quality conditions (Reid, 1961). In acidic streams, such as might be expected downstream of ombrotrophic bogs, the filamentous algae Mougeotia is often prominent (Haines, 1981), while acidophilous diatoms and blue-green algae may also be abundant (Hendrey and Vertucci, 1980). Rooted plant communities in streams may be diverse, and include several classes of plants. Primary producers provide a source of energy for consumer

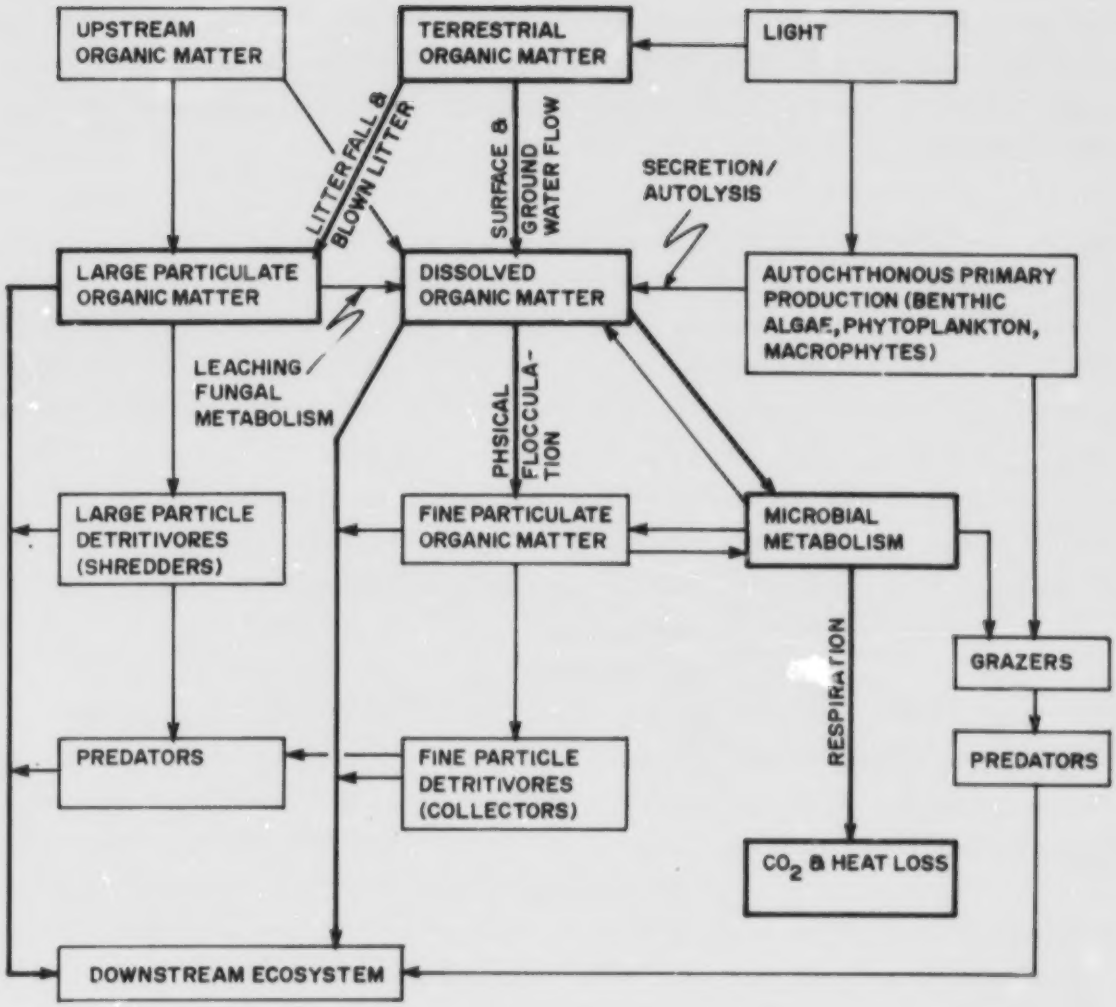


Figure **12**

Model of an Idealized Stream Ecosystem

organisms, and aquatic macrophytes provide feeding surfaces and in-stream cover for many species of fish and invertebrates. Primary productivity in Canadian freshwaters is usually limited by the availability of plant nutrients, particularly phosphorus, and light (Wetzel, 1975).

Benthic assemblages may be diverse, depending upon food availability and physico-chemical conditions. Important components of the benthos include aquatic insects, crustaceans, molluscs and annelids. These organisms are important in the diets of many fishes. In acidic streams, certain groups such as immature mayflies and stoneflies, molluscs, oligochaetes, crayfish and amphipods may be uncommon or absent (Haines, 1981). Friberg et al. (1980) found that in acidic streams (pH 4.3-5.9), benthic scrapers were less abundant and benthic shredders more abundant than in neutral streams (pH 6.5-7.3), suggesting a decrease in the availability of periphyton for consumption by scrapers. Benthic communities may be sensitive to alterations in pH, organic matter, productivity and suspended solids levels.

Fish communities in streams and rivers vary according to zoogeographic, physical, chemical and biological constraints. Many species are economically valuable as commercial or sport fish. Species such as the centrarchids (sunfishes, crappies, basses), yellow perch (Perca flavescens), muskellunge, northern pike, bullheads and many of the cyprinids (minnows) occur most commonly in larger, slow-flowing streams. Walleye (Stizostedion vitreum) and suckers primarily inhabit large streams and lakes, but may enter smaller streams for spawning. Several minnows are most common in small streams and creeks. Of these, creek chub, finescale dace, pearl dace, fathead minnow and northern redbelly dace are common in humic-stained waters draining boggy areas. The brook stickleback and the central mudminnow are frequent inhabitants of small, slow-flowing streams (Scott and Crossman, 1973).

Several salmonid species are permanent or temporary residents of streams and rivers in peatland watersheds. Essentially, all riverine salmonids rely on clear, gravelly streams and rivers for spawning. Brook trout (Salvelinus fontinalis) occur in brown-water streams throughout eastern Canada and have a spotty distribution in all provinces west of Ontario (Scott and Crossman, 1973). They may remain permanent residents of cool, well oxygenated streams and rivers, or may migrate to sea or into lakes. Of all the salmonids, brook trout appear to be most tolerant of low pH conditions encountered in peatland

drainage areas. Brown trout (Salmo trutta) have habitat requirements similar to those of brook trout, but are confined mainly to southern Ontario and southern Alberta. Other species are generally anadromous, leaving the sea or large lakes for spawning streams at maturity. These species include Atlantic salmon (Salmo salar), rainbow trout (Salmo gairdneri), arctic char (Salvelinus alpinus), and five Pacific salmon (Oncorhynchus) - pink (O. gorbuscha), chinook (O. tshawytscha), coho (O. kisutch), sockeye or kokane (O. nerka) and chum (O. keta). After hatch, juveniles of the anadromous species spend variable periods in spawning streams, from weeks to a few months for Pacific salmon, to an average of three years for Atlantic salmon (Scott and Crossman, 1973). In many areas, landlocked populations of anadromous species have been established.

7.2.2 Lake Ecosystems

Lakes may occur virtually anywhere in a watershed, and may receive peatland drainage either directly, or indirectly via inflowing streams. Important morphometric variables influencing the development of lentic communities include mean and maximum depth and flushing rate. Shallow lakes with high flushing rates may support communities similar to those of large, slow-flowing rivers. Deep lakes usually stratify in summer into a surface layer of relatively warm water (epilimnion) and a bottom layer of colder water (hypolimnion), with the two layers separated by a thermocline (metalimnion). These lakes usually support a distinct community in each layer. Lakes are sedimentary environments, and act as "sinks" for inorganic and organic matter (including contaminants) transported from upstream waters.

Lakes are frequently classified by limnologists according to their trophic status. Oligotrophic lakes are usually deep and clear, and have low rates of primary productivity due to low concentrations of inorganic nutrients (especially phosphorus). These lakes usually maintain an oxygenated hypolimnion throughout the year, since rates of organic decomposition in bottom waters and sediments are low. At the other extreme, eutrophic lakes are rich in nutrients and have high rates of primary productivity. The process of eutrophication in lakes is natural, and occurs over geologic time frames due to infilling by watershed materials. Peatland discharge is a significant natural source of nutrient input to nutrient-poor lakes (Crawford, 1978). The eutrophication process may be greatly accelerated by man through the introduction of phosphorus in sewage and other waste. Eutrophic lakes often develop an anoxic hypolimnion in summer, due to high rates

of organic decomposition in bottom waters and sediments. Mesotrophy is the intermediate condition between oligotrophy and eutrophy. Dystrophic lakes have low rates of primary productivity, but high rates of organic accumulation due to inputs of allochthonous materials. Dystrophic lakes may develop over time into bogs or terrestrial environments.

Organic matter in lakes is produced by phytoplankton, rooted macrophytes and attached algae. Allochthonous organic matter is introduced to lakes mainly by inflowing tributaries, and is less important in the metabolism of most lakes than in stream ecosystems. Phytoplankton is produced in surface waters down to the depth where light becomes limiting. Macrophytes and attached algae are important in the littoral zone where sufficient light for plant growth reaches the lake sediments. In shallow lakes, the littoral zone may occupy the entire lake while in deep lakes, it is usually confined to a narrow band around the perimeter. In Shield lakes, many of which drain ombrotrophic peatlands, primary productivities are low due to low nutrient concentrations, high concentrations of humic materials and frequently considerable lake depths. In such lakes, micro-flagellate species such as several of the Chrysophyceae may predominate, due to their advantageous high surface area to volume ratio and mobility (Janus and Duthie, 1979). It appears that in brown-water lakes, phytoplankton production based on heterotrophic use of humic matter may be as important as photosynthetic production (Ostrofsky and Duthie, 1975). In more acidic lakes, the numbers of phytoplankton species are usually reduced, although biomass and productivity may be comparable in acidic and non-acidic lakes with similar nutrient levels.

Important primary and secondary consumer groups in lentic environments include zooplankton and benthos. Zooplankton includes microcrustaceans and rotifers. In more acidic lakes, such as in some areas draining bogs, zooplankton densities are relatively low with few dominant species (typically Bosmina, Diaptomus or Keratella species; Haines, 1981). Important components of the lake benthos include crustaceans, aquatic insects, molluscs and annelids. Certain groups are more sensitive to acidic conditions than others, as noted earlier (Section 7.1). These smaller consumer organisms provide the food base for the fish community.

Fish communities include coldwater species, confined primarily to the hypolimnion in summer, and warmwater species found in the epilimnion. Coldwater and warmwater

species are more dispersed from autumn to spring when water temperatures are low and temperature differences with depth are small. Coldwater species are often absent in eutrophic lakes where the hypolimnion becomes oxygen-deficient in summer. Most of those species occurring in lotic environments, including the salmonids, may be found in lakes either seasonally or throughout the year. Common lake fish include lake trout (Salvelinus namaycush), rainbow trout, brook trout, whitefish (Coregonus spp.) (coldwater species), walleye, yellow perch, northern pike, muskellunge, centrarchids and suckers (warmwater species), as well as several smaller species of forage fish. In addition to these, many of the landlocked and anadromous salmonids are seasonally resident in, or migrate through, lentic environments.

7.2.3 Estuarine Ecosystem

Streams and rivers eventually empty into the ocean through estuaries, either by direct discharge, or via larger freshwater basins such as the Great Lakes. Peatlands may discharge directly into an estuary in coastal areas. In the estuary, freshwater is mixed with seawater through the combined effects of stream flow, tides and wind-driven currents. Salinities range from freshwater conditions in the upper estuary to seawater conditions in the lower estuary, and may fluctuate widely depending on variations in freshwater inflow and mixing processes. The effects of peatland drainage in the estuary may be imperceptible, due to rapid dispersion and dilution, and buffering by seawater.

The aquatic communities of estuaries include marine species and freshwater species, depending on the relative proportion of seawater and freshwater, and on the instability of salinity conditions due to mixing processes. Relatively few freshwater or marine species are found in brackish waters where salinity conditions may vary widely. However, commercially important anadromous species migrate through estuaries of spawning rivers and are exposed to any contamination introduced to these rivers.

7.3 Biological Response to Runoff from Undisturbed Peatlands

Impaired runoff water quality and subsequent impacts on downstream aquatic communities are perceived as major environmental issues relating to peatland development. However, preliminary field observations and laboratory studies indicate that drainage from undisturbed peatlands may, in itself, represent a stressful or toxic

environment to certain groups or species of aquatic organisms (i.e., Crawford, 1978). It is therefore essential that the effects of peatland drainage on aquatic biota be identified before mining impacts are superimposed.

A preliminary method of assessing the amount of stress placed on aquatic organisms by their physico-chemical environment is through comparison of peat runoff water quality to Federal or Provincial Objectives for the Protection of Aquatic Life (i.e., Ontario Ministry of the Environment, 1978; McNeeley et al., 1979; International Joint Commission, 1978, 1980). Objectives are derived from quantitative evaluation of biotic and abiotic factors which govern the influence of individual parameters on the most sensitive organism likely to be affected. They may be considered to represent the minimum acceptable level of water quality. Table 20 lists water quality objectives for parameters commonly discharged in peatland drainage.

The target species used in developing objectives is either man, or aquatic species considered to be of economic or ecological importance (i.e., Rainbow Trout, Fathead Minnow, Daphnia magna). Factors considered in deriving regulatory criteria routinely include acute and chronic toxicity, carcinogenicity, persistence, bioaccumulation potential, aesthetics, and other considerations. Objectives apply to specific compounds, elements or physico-chemical properties which have been shown to affect the quality of aquatic life. They are by no means comprehensive, nor do they account for antagonistic, synergistic or additive effects of chemical mixtures.

Discharge waters from undisturbed peatlands routinely exceed Water Quality Objectives for pH, dissolved oxygen, nutrients and metals. In general, bog water quality is poorer than fen water quality. The potential impacts of these parameters on aquatic communities are discussed below.

7.3.1 pH and Acidity

As shown in Table 20, the optimum pH for aquatic life is 6.5 - 8.5. Thus, undiluted waters from bogs and poor to intermediate fens exert an acid stress on many aquatic organisms. This is clearly illustrated through the low species diversity and absence of certain groups from peatland drainage areas. Only acid-tolerant species or individual populations which have, over a long period of time, become acclimatized to acidic

TABLE 20: FEDERAL WATER QUALITY GUIDELINES FOR THE PROTECTION OF AQUATIC LIFE (ONTARIO MINISTRY OF THE ENVIRONMENT, 1978; McNEELEY ET AL., 1979; INTERNATIONAL JOINT COMMISSION, 1980) (all values in mg/L unless otherwise specified)

Parameter		Guideline or Objective	
pH (unitless)		6.5 - 8.5	
Alkalinity (as $CaCo_3$)		- not to decrease by more than 25% of the natural concentration	
Ammonia *		0.02	
Dissolved Oxygen: (% Saturation)	Temperature (°C)	Cold Water Biota	Warm Water Biota
	0	54	47
	5	54	47
	10	54	47
	15	54	47
	20	57	47
	25	63	48
Hydrogen Sulfide		0.002	
Phenols		0.001	
Total Phosphorus	lakes	0.020	
	streams	0.030	
Temperature		- not to exceed ambient temperature by more than 10°C	
Total Dissolved Solids		- not to exceed ambient conditions by more than 1/3	
Turbidity		- not to change by more than 10%	
Metals:			
Arsenic		0.100	
Beryllium		0.011	
Cadmium		0.0002	
Chromium		0.100	
Copper		0.005	
Iron		0.300	
Lead (alkalinity dependent)	Alkalinity	Maximum Pb Concentration	
	0 - 20	0.005	
	20 - 40	0.010	
	40 - 80	0.020	
Mercury (filtered water)		0.0002	
Nickel		0.025	
Selenium		0.100	
Zinc		0.030	

* Ammonia in un-ionized form (NH_3).

TABLE 20a: PERCENTAGES OF UN-IONIZED AMMONIA (NH_3) AQUEOUS AMMONIA SOLUTION (ONTARIO MINISTRY OF THE ENVIRONMENT, 1978)

Temperature	pH				
°C	6.0	6.5	7.0	7.5	8.0
5	0.013	0.040	0.13	0.39	1.2
10	0.019	0.059	0.19	0.59	1.8
15	0.027	0.087	0.27	0.86	2.7
20	0.040	0.13	0.40	1.2	3.8
25	0.057	0.18	0.57	1.8	5.4
30	0.081	0.25	0.80	2.5	7.5

conditions are present. The latter phenomenon is of particular interest since it explains the occurrence of reproducing populations of certain salmonid species, such as Brook Trout, Atlantic Salmon and Arctic Char in ombrotrophic bog lakes and streams of Cape Breton Island, Nova Scotia and northwestern Newfoundland (BEAK, 1976; 1980a; DeGraaf, 1983). The pH in these systems ranges from 4.0 - 4.9. This work is corroborated by studies in Wisconsin (Rahel, 1983; Rahel and Magnussen, 1983). Studies of acid rain-impacted systems report that salmonids are extirpated at pH 4.7 - 5.0 (Schofield, 1976; Harvey, 1979; Harvey et al., 1981; Watt et al., 1983). It therefore appears that in systems in which buffering capacity is controlled by organic acids, increased pH tolerance may occur. Although further studies are required, these results are potentially important in assessing the potential aquatic impacts of peat mining since they imply that:

- o populations which are acclimatized to low pH arising from naturally acidic conditions may be more resistant to further alterations in pH,
- o equivalent pH's in mineral acid-dominated systems and organic acid-dominated systems do not exert equivalent toxic effects and should therefore not be directly compared.

These findings also raise questions as to the impact of acid precipitation on peatland areas. Economically important peatlands in Nova Scotia, New Brunswick, Quebec and southern Ontario are located within the zone of influence of acid precipitation. Reductions in fish populations have been reported in these areas (Bangay and Riordan, 1983). However the interraction between mineral and organic acids and resultant mortality have not been studied.

Nonetheless several investigators have shown that bog waters are toxic to aquatic biota. The toxic response is generally considered to be related to high concentrations of humic substances in bog water (Crawford, 1978; King et al, 1980). In bioassay tests, undiluted bog water evoked toxic and avoidance responses in fish from receiving waters. Geisler et al. (1971) demonstrated that characids and cichlids were sensitive to humic substances from bog water, and that this sensitivity did not appear to be related to pH. Johnson and Hasler (1954) noted that growth was inhibited in fish from blackwater lakes draining peat bogs in Wisconsin, and that this growth inhibition could not be entirely eliminated by fertilizing the lake water. Bog-derived organic compounds also appear to

be toxic to aquatic insect larvae (Janzen, 1973) and algae (Livingston, 1905). However, a number of studies have shown that humic acids reduce metal and polyaromatic hydrocarbon toxicity through complexation (Zitko et al., 1973; Leversee et al., 1983; Ray, 1983).

There are no water quality objectives or standards for organic acids found in peat waters, and the specific toxicities of these compounds are poorly known. Further baseline research in this area is required before their potential impact in discharges from mining can be accurately ascertained.

7.3.2 Dissolved Oxygen

Aquatic biota have varying minimal dissolved oxygen requirements, depending not only on species, but also on life stage, temperature and acclimatization. Below a critical threshold level, the animal will suffer respiratory distress and may die, or be driven from the affected area to more favourable conditions (Davis, 1975).

Biochemical oxygen demand (BOD) and chemical oxygen demand (COD) are measures of the oxygen required to oxidize various compounds. BOD measures the amount of oxygen required for the biochemical degradation of organic matter and the oxidation of various inorganic components such as sulphides and ferrous iron. COD measures susceptibility to a strong chemical oxidant. Waters of high BOD and COD content may readily become deficient in oxygen, depending on the rate of oxygenation at the air-water interface. Oxygen-deficient waters are unable to support many sensitive species of aquatic biota. Most economically desirable freshwater fish species are sensitive to low oxygen conditions.

Within the watershed, dissolved oxygen concentration depends upon the dynamic balance between oxygen sources and sinks. Oxygen enters a stream or lake via atmospheric exchange, inlet streams and photosynthesis. Processes removing dissolved oxygen include stabilization of organic compounds by bacterial action, stabilization of chemical compounds by chemical oxidation, respiration by aquatic organisms, respiration in the sediments, and the bacterial conversion of ammonia to nitrate. Carbonaceous materials introduced by peat drainage may remain suspended or dissolved in the water column, or may settle to the sediments, in either case resulting in a total increase in the oxygen demand of the system.

7.3.3 Nutrients

Phosporus and nitrogen are the two most important plant nutrients in freshwater systems (Wetzel, 1975). While these elements are essential to all aquatic life, excessive concentrations may cause eutrophication. The resultant increased rates of photosynthesis and respiration can lead to widely varying dissolved oxygen concentrations and may cause the hypolimnia of lakes to become anoxic, leading to the demise of important coldwater fishes. Furthermore, eutrophication may cause unsightly growths of aquatic weeds and algae, reducing the recreational value of the system.

Waters from peatlands may contain relatively high total nutrient concentrations. Verry (1975) reported mean total phosphorus (TP) and total nitrogen (TN) concentrations of 0.6 and 1.34 mg/L for perched bogs and 0.29 and 0.58 mg/L for groundwater fens in Minnesota. In Scandinavian bogs, Gorham (1955) reported a range of TP of 0 to 0.149 mg/L, with most values exceeding 0.1 mg/L, and a range of TN of 1.6 to 8.72 mg/L. However, productivity is directly related to the concentration of bioavailable nutrient forms. Crawford (1978) examined the effect of Minnesota bog water on growth and photosynthetic activity of a number of algal species and found that stimulation was logarithmically proportional to the amount of bog water added. Further experiments revealed that nutrient bio-availability was controlled by the bacterial beakdown of particulate organic forms into dissolved forms.

It appears that primary productivity in bog water drainage systems may be either N- or P- limited. An N:P ratio of 15:1 is normally required by primary producers in freshwater systems, and a ratio exceeding this generally indicates that P is limiting (Dillon, 1974). Verry's (1975) studies of Minnesota peatlands reveal N:P ratios of 2.2:1 and 2.0:1 for perched bogs and fens, respectively. This indicates that nitrogen is the limiting nutrient in these systems. However, atmospheric nitrogen is readily transferred to the water column by various biogeochemical processes, and thus nitrogen limitation is not anticipated to be of major concern in peatland watersheds. On the other hand, Gorham (1955) reported N:P ratios of at least 50:1 in Scandinavian bogs. Primary productivity in northern temperate lakes in Canada is likewise considered to be generally P-limited (Dillon, 1974; Wetzel, 1975).

High nitrogen concentrations, commonly reported in peatland runoff, may also represent a potentially toxic input to downstream aquatic communities. The un-ionized form of ammonia (NH_3) is strongly toxic to aquatic organisms (Rankin, 1979). Under the strongly acidic to slightly acidic conditions in ombrotrophic and weakly minerotrophic systems, respectively, ammonia is present almost entirely in non-toxic ionized form (NH_4^+). Under these conditions, concentrations of NH_3 are orders of magnitude less than the 0.02 mg/L concentrations considered safe for aquatic life. However, as shown in Table 20a, should downstream pH or temperature increase, the same total nitrogen concentrations could present a potential hazard to aquatic life.

7.3.4 Trace Elements

As discussed in Section 5, the low ambient pH of ombrotrophic peatlands causes the solubilization of many metals. These are potentially leached from the peat complex in dissolved or particulate form and discharged to aquatic receiving environments. Comparison of typical peat runoff water chemistry concentrations with water quality guidelines reveals that several metals commonly exceed desirable concentrations for the protection of aquatic life (Table 20).

These include:

- aluminum
- cadmium
- copper
- iron
- lead
- mercury
- nickel
- zinc

Heavy metal toxicity in peatland drainage waters has not been studied. However it is possible that toxic effects attributed to pH or humic substances (i.e., Crawford, 1969) could also be related to metal toxicity. For example, recent acid rain-related research indicates that at pH 4-6 certain aluminum forms are toxic to aquatic organisms (Everhart and Freeman, 1973; Baker and Schofield, 1980; Grahn, 1980). On the other hand organo-metallic complexing may reduce metal toxicity.

7.3.5 Toxicity

As indicated in the preceding sections, the response of aquatic organisms to drainage from undisturbed peatlands has been largely unstudied. The relatively low net primary productivity and species diversity indicate that naturally acidic environments are stressful to aquatic life. However acid-tolerance and acclimatization apparently occur. Further investigations into the biological response of aquatic organisms is required if developmental impacts are to be accurately predicted.

8.0 AQUATIC IMPACTS OF PEATLAND DEVELOPMENT

Downstream aquatic environments may be highly susceptible to adverse impacts from peat mining. Any combination of streams, rivers, ponds, lakes and estuaries may be affected. Many peatlands occur in headwater areas where watersheds may be more sensitive to disturbance due to relatively low stream and lake discharge volumes. At the other extreme, coastal peatlands may drain directly into estuaries through short channels or via small watersheds.

The effects of peat mining on aquatic ecosystems can be divided into hydrologic and water quality impacts.

8.1 Hydrology

8.1.1 Effects on Water Yield and Discharge Rates

The hydrological impact of peat mining is determined by a number of factors relating to the water balance characteristics of the peatland, the physical properties of the peat, and the choice of mining technique. No published accounts of such impacts arising from wet mining are currently available however considerable controversy exists concerning the hydrological impacts of peatland drainage and dry mining. The literature contains conflicting reports of both increases and decreases in discharge volumes and rates (i.e., Burke, 1968; Heikurainen et al., 1978; Seuna, 1981), and much effort has been expended in attempts to prove that one or the other is more characteristic. In fact, it appears that both types of impacts occur. The nature and magnitude of hydrological alterations can be predicted through characterization of the hydrodynamic balance of the system.

Reliable calculations of runoff from both undisturbed and disturbed peatlands can be made using the water balance equation, described in Section 2.1, and presented again below:

$$P + I - D - V - E - \Delta S = 0$$

Where,

P = precipitation

I = inflow

D = discharge through groundwater
ΔS = storage capacity of the peatland
V = vertical seepage to deep subsurface layers
F = evaporation

In ombrotrophic systems, I approaches 0, and V is negligible relative to the other parameters. Solving for D, the equation becomes,

$$D = P - E - \Delta S$$

Therefore, the nature and extent of hydrological impacts is determined by the net change in evaporation and storage relative to undisturbed conditions. The magnitude of change of these components is influenced by several factors, including:

- mining technique
- size of mining operation
- location of the peatland within the watershed
- physical properties of the peat
- season
- time from commencement of mining

Significant differences in hydrological impacts occur between mining techniques. Dry mining requires lowering the water table through drainage; wet mining does not.

Dry Mining

In dry mining the bog is cleared of vegetation and the water table is then lowered through installation of a ditch system. Drainage water is collected in perimeter ditches and discharged through an outflow(s). The ditches are progressively deepened as the surface peat is dried and harvested, until the bog has been mined to the maximum desirable depth.

Most published reports agree that dry mining results in a net increase in total water yield and maximum discharge rate, but impacts on minimum discharge rates and stormflow are less well defined (Seuna, 1981; Brooks et al., 1982).

Changes in evaporation and storage capacity are associated with each major step of the mining procedure. Vegetation removal results in a large decrease in evapotranspiration. Since evapotranspiration accounts for up to 90% of total annual evaporation, this results in a considerable decrease in total evaporation (Eggelsmann, 1964; Bay, 1968). Increases in direct evaporation arising from increased solar radiation, wind turbulence and decreased albedo occur, but seldom offset the net evaporative loss (Brooks and Predmore, 1978). As a result, less water is removed from the peatland to the atmosphere during spring and summer. Therefore, storage capacity decreases and surface runoff potential increases.

Loss of ground or canopy cover also results in increased discharge. Heikurainen (1976) notes that tree-cover acts as an insulator, causing a delay in spring runoff. Likewise ground cover protects against deep frost penetration. Removal of vegetative cover leads to increased frost penetration, decreased infiltration, and subsequently, higher surface runoff. Changes in microrelief through grading decrease water storage capacity (Brooks and Predmore, 1978).

The purpose of drainage is to lower the water table and thereby decrease the moisture content of the surface peat. The ultimate hydrological effect is generally an increase in both the maximum volume and rate of discharge due to increased surface runoff. Minimum discharge may also increase due to reduction in evaporation and slower flow through the peat, but cases of decreased minimum flow have also been recorded. Hommik and Madisson (1975) report that base flow in fens may also be increased through drainage. Since peat is generally less than 10% solids by volume, drainage has the immediate effect of decreasing porosity which results in subsidence. Other related physical parameters such as bulk density and compaction also increase, and in addition, aerobic conditions created by drainage of the surface peat stimulate microbial decomposition. The net result is denser peat with higher water retention capacity and lower hydraulic conductivity. Both of these conditions lead to decreased storage capacity, and potentially higher surface runoff.

The amount of subsidence is dependent upon the initial humification of the peat and the intensity of drainage. Undecomposed peats show greater subsidence than highly humified peats. Drainage intensity determines the ultimate height of the water table and is dictated by the spacing and depth of ditches. Obviously closer deeper ditches increase

discharge. The drained water table takes on a convex shape, with an increasing hydraulic gradient towards the ditches.

Drainage characteristics are altered as peat extraction proceeds. Typical energy peat profiles consist of undecomposed peat underlain by more humifed peat. As the peat is removed the denser peat becomes the surface peat. Consequently, while subsidence decreases, the higher bulk density and water retention capacity of the peat causes a decrease in hydraulic conductivity and storage capacity which leads to higher surface runoff.

Some controversy exists concerning the influence of peatland drainage and mining on stormflow response. There are basically two views. The first contends that peatland drainage decreases the duration of peak flow but increases the flow peak (Ahti, 1980; Brooks et al., 1982). The second suggests that the duration of peak flow is increased but the peak flow rate is decreased (Burke, 1973; Heikurainen et al., 1978). These differences appear to be related to the slope and location within the watershed of the peatland, the hydraulic conductivity of the peat and the intensity of ditching.

Few quantitiative hydrological investigations of peat mining operations exist, although some parallels from the extensive European forestry drainage literature may be drawn. On-going studies in northern Minnesota are perhaps most directly applicable to climatic conditions in boreal regions of Canada. In these studies, Brooks et al. (1982) compare water yields and discharge rates of an actively mined horticultural peat bog to a nearby undisturbed bog. Unfortunately mining operations had already been on-going for 24 years prior to the initiation of the study. The results therefore reflect long-term impacts.

As shown in Figure 13, the mined bog has a higher total runoff and a greater percentage of flow in the first half of the year (January - June) than the control bog. Streamflow response in both systems is dominated by snowmelt.

Stormflow analyses based only on rainfall events show that groundwater seepage and soil moisture strongly influence flood response. However, in general, the mined bog exhibits a shorter lag time and higher peak discharge rate, than the undisturbed bog, although total storm flow volumes are similar.

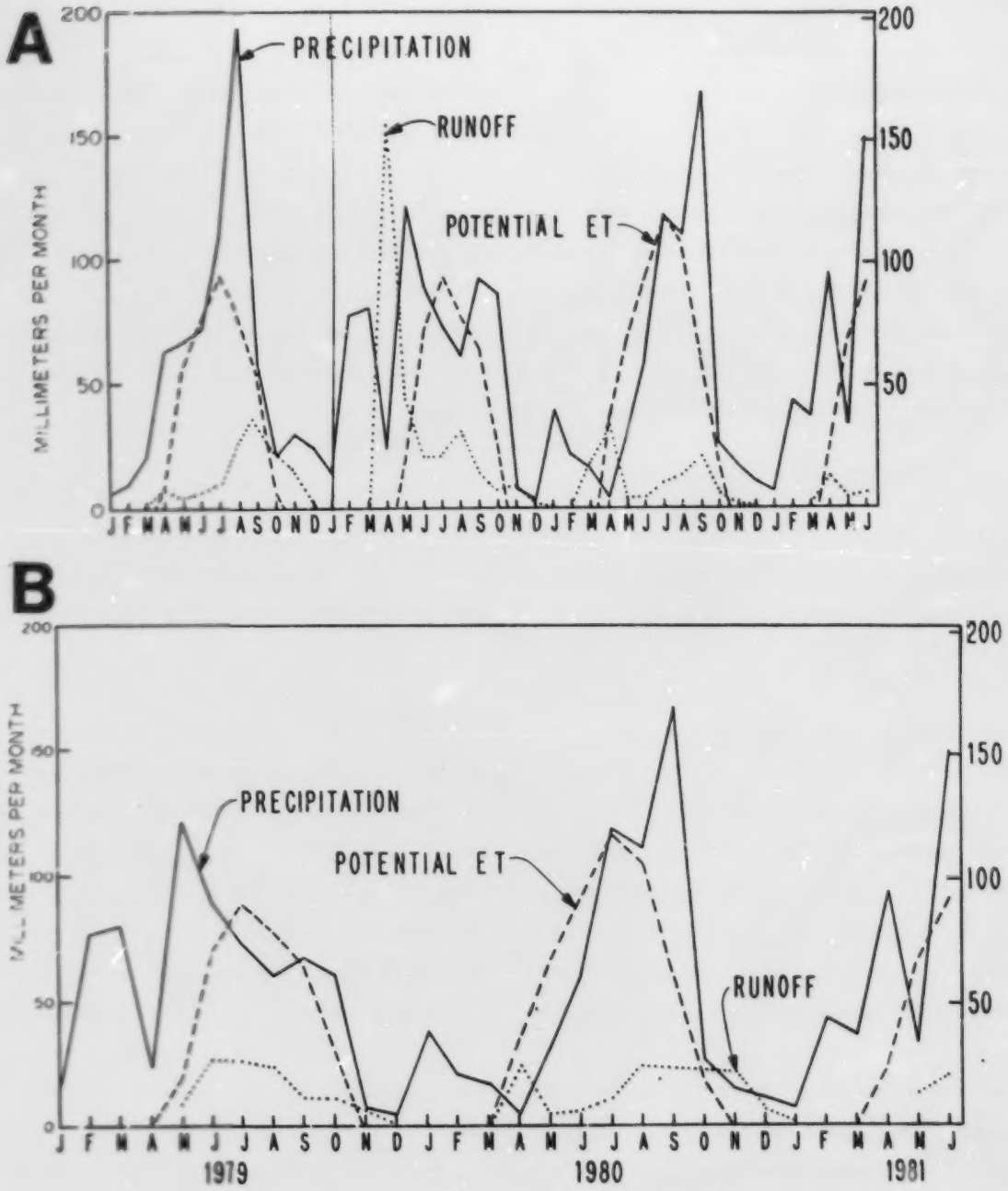


FIG. 13 COMPARISONS OF MONTHLY WATER BUDGETS FOR MINED BOG (A) AND CONTROL BOG (B) (modified from Brooks et al., 1982)

Sallantaus and Patila (1983) monitored the runoff from ombrotrophic peatland watersheds in southern Finland during a 1-2 year period following drainage for peat mining. The peat profile consisted of undecomposed Sphagnum at the surface underlain by sedge peats to depths of up to 6 m. The sites were cleared and drained during the winter and early spring. Ditches were 1.5 metres deep, spaced at 20 m intervals. During the first year following drainage total runoff from the mined sites was approximately two times greater than typical runoff from undisturbed bogs in the area (Kaitera, 1971). Peak flows occurred during the spring, immediately following drainage, however summer and winter low flows were also higher. The increased runoff was attributed to decreased water storage capacity resulting from subsidence. At one location the bog surface elevation decreased by 180 mm within five months of drainage.

Extensive studies of peatland forest drainage have been conducted in Finland and other parts of Europe. These studies are of limited applicability to peat mining since neither vegetation or peat is generally removed, and hence hydrological effects are due largely to drainage. Nonetheless, they provide insight into water balance relations and temporal trends.

Seuna (1981), working in southeastern Finland, observed a 43% increase in mean annual runoff during an 8 year period following drainage of an open bog/swamp complex. Over two-thirds of the recorded increase was directly attributable to decreased evapotranspiration, although tree and ground cover were not disturbed. However, the lowered water table and subsequent drying of the surface peat did not allow capillary uptake. Consequently the effective storge capacity of the peatland decreased. Nine to eighteen years after drainage, annual runoff averaged 18% higher than the control site. Total runoff approached pre-drainage conditions approximately 20 years after drainage.

Statistically significant increases were also observed in spring and summer maximum runoff during the first few years after drainage, but were approximately equal to, or lower than, runoff from the control site during the 10-20 year post-treatment period. Miminum runoff for both summer and winter also increased signficantly in the 10 years following drainage. Some decrease was observed over time but since the ditches had been dug to the porous sandy mineral layer, minimum discharge continued to exceed that of the undrained area, even after 20 years.

Studies by Heikurainen et al. (1978) and Heikurainen (1980) in forested peatlands in northern Finland show that, in some cases, the water storage capacity of the peat may be increased by drainage. Maximum spring runoff rates were observed in undrained bogs, although runoff from drained sites was of longer duration. Peak discharge during the summer was related to precipitation patterns. During dry years, runoff from the drained peatland was higher, but during wet summers average runoff from the undrained peatlands was higher. However, the drained catchments exhibited greater stormflow peaks due to surface runoff than the undrained bogs. Based on these results the authors concluded that drainage exerts a levelling effect on runoff peaks.

Wet Mining

In wet mining, the site is cleared but not drained. Peat is removed at field moisture by a dredge or similar piece of equipment and transferred as a slurry by pipeline to a dewatering plant. The process water is then, generally, returned to the bog (Monenco,1981). Thus a shallow pond is produced at the mine site.

Theoretically the hydrological impacts of wet (hydraulic) mining should be less severe and more easily controlled than impacts from dry mining since the water balance is not as radically altered. However there is currently no available data to support this.

The magnitude of hydrological impacts will depend on the presence or absence of an outlet or retention dam and regulation of outflow. Water levels in the pond will be regulated by the balance of inputs and losses due to evaporation and outflow. Inputs will include precipitation, process water and seepage from the surrounding peat. Removal of peat, and influx from surrounding areas will increase the storage capacity of the mined peatland. Evaporation from the free water surface will likely exceed evapotranspiration. Thus under normal conditions the water balance within the ponded area will be relatively stable, and runoff will be regulated by the height of the outfall.

The potential for flash flooding exists if stormflow causes the pond to overflow. Once total storage capacity has been reached, the rate of free water movement will be very rapid.

Pond siltation could also influence water balance. Continuous exchange between the pond and surrounding peat would allow maximum utilization of storage capacity. However, the dewatering effluent may contain high concentrations of fine suspended materials. If returned to the pond, these could potentially clog pore spaces and create an impermeable seal. Runoff would then be regulated strictly by precipitation, effluent inputs and evaporative losses.

8.1.2 Biotic Response

Biotic response to any alteration in watershed flow regimes will depend on the degree of alteration. Enhancement of extremes in flow conditions is generally undesirable, since both low flow and peak flow conditions may be detrimental to may organisms. Reduction in stream flow may discourage rheophilic (current loving) species; increased flow may adversely affect species requiring low flow conditions. Any signficant alteration in the runoff response of peatlands may therefore be expected to reduce the diversity of the aquatic community. Mauch (1963) observed, in some sections of the Moselle River (Germany), that silt collects during low flow, creating conditions unsuitable for riverine benthos, while during peak flows sediments are washed away and conditions are too unstable for species requiring slow currents. Hynes (1970) noted that fast water may preclude colonization by fish requiring slow currents, while flash floods may be deleterious even to swift-water species such as trout.

Spawning on flooded areas followed by receding water levels may result in the death of eggs and young of certain fishes (Hynes, 1970). On the other hand, some species such as the bigmouth buffalo, in Saskatchewan's Qu'Appelle River, only spawn successfully during years of high discharge (Johnson, 1963). Extremely low flow conditions may result in dessication of potential spawning habitat.

Impacts of an altered hydrologic regime on biological communities are generally assessed on the basis of known environmental requirements of important community components such as commercial or sport fishes. For example, quantitative measure of areal loss of salmonid spawning or rearing habitat may be used to predict losses in recruitment of adult populations, based on the assumption that loss of habitat units and loss of recruitment are proportional. Site-specific data concerning fish productivity of the undisturbed systems is also required for this type of analysis (e.g., Ricker, 1975). This

and similar approaches have been widely used in evaluating salmonid habitat loss due to flow manipulation.

8.2 Water Quality

Degradation of runoff water quality and subsequent impacts on downstream aquatic ecosystems is perceived as one of the major environmental issues relating to peatland development. However the small amounts of quantitative baseline and impact-related data currently available, preclude realistic impact evaluation at the present time. While any alteration in outflow water chemistry could potentially influence downstream aquatic communities, positive or negative impacts depend on the sensitivity of the system. Preliminary impact assessment should therefore focus on the potential for further alteration of those parameters which limit aquatic productivity in undisturbed peatland watersheds as well as any other parameters which might be elevated to unacceptable levels as a result of the mining operation.

8.2.1 Changes in Water Quality

Water quality impacts associated with peat mining are discussed in a number of publications (i.e., King et al., 1980; Carpenter and Farmer, 1981). Many of these appear to be based on "sound ecological reasoning", however, until they have been adequately field-tested, questions relating to the relative sensitivity of different peatland types, and biotic response cannot be answered. Nor can effluent regulations or mitigative measures be formulated.

There are a few field accounts of water quality variations associated with peatland drainage and/or mining which give some indication of the parameters of concern (ie: Brooks et al., 1982; Sallantaus and Patila, 1983). However all studies are based on small drainage areas and do not give complete long-term observations throughout the pre-development, development and post-development phases.

Differences in the types and magnitudes of impacts reported between studies clearly indicate the importance of site-specific factors such as:

- topography and climatic conditions
- peatland type and location within the watershed
- surface and groundwater input
- seasonal variability in physico-chemical parameters.

In the following sections pertinent field observations of the water quality impacts of wet and dry mining are summarized. Based on these very preliminary studies it appears that impacts associated with wet mining cause less disruption of the hydrological regime and are more easily controllable than potential dry mining impacts.

Dry Mining

The studies of a Minnesota horticultural peat mine (Brooks et al., 1982) and a Finnish peat mine (Sallantaus and Patila, 1983), previously described in Section 8.1.1, reveal changes in a number of similar water quality parameters, although the magnitudes of the variations differ considerably. This is likely because the Minnesota study site had been drained and mined for 20 years prior to monitoring, while the Finnish observations were from a recently drained site.

Both studies reveal increases in suspended and dissolved solids and nutrients. Sallantaus and Patila (1983) report average suspended sediment loadings of 500 kg per drained hectare during drainage. Maximum loadings occurred during peak flows, and the specific sediment discharge during the six months following the commencement of drainage was twice as high as the annual average from similar undisturbed peatland watersheds (Kauppi, 1975). After the initial drainage period, average suspended sediment concentrations dropped to 10 mg/L. This value is similar to the Minnesota average runoff concentration (13.7 mg/L) which may be considered representative of long-term conditions. Brooks et al. (1982) note that while this value is low, it is nonetheless significantly higher than background levels (5.1 mg/L).

On a volumetric basis, most of the particulate material will be organic. However if the bog is ditched to the zone of influence of mineral substrate, as was the case in the Finnish study, the drainage waters may contain significant amounts of inorganic material (ie: silt, clay).

Nitrogen and phosphorus concentrations were also higher in the mined bog runoff in both studies. At the Finnish site, flow-weighted averages of inorganic nitrogen (primarily NH_4^+ increased 10 to 100-fold during the 15 month period following drainage, from a background concentration of 30 mg/L. Similarily, total phosphorus concentrations increased from a pre-mining average of 18 mg/L to 30-200 mg/L following drainage. Background nutrient concentrations in the Minnesota bog were much higher than in the Finnish bog (NH_4^+=1.30 mg/L, TP = 80 mg/L). While significant increases in both NH_4^+ and TP were observed in the mined Minnesota bog, the magnitude of change was at the time of measurement (ie: 20 years after drainage) much less than in the recently drained Finnish bog. Organic nitrogen concentrations were also found to be significantly higher in the mined (Minnesota) bog, however it is interesting to note that nitrate (NO_3 + NO_2) concentrations were not.

A major difference between the Minnesota and Finnish studies relates to the impact of mining on acidity. In the Minnesota bog, mining produced significant increases in acidity-related parameters such as (acidity), colour, exchangeable cations, iron and aluminum, humic and fulvic acid concentrations, and a decrease in pH. However, in the Finnish study, the pH of the discharge increased after mining. This was attributed to deep ditching which increased runoff from the deeper peats located closer to the mineral layer.

Heavy metal concentrations were also estimated in the Minnesota study. No long-term differences were found in the concentrations of toxic metals (Cu, Zn, Ni, Pb, Cr, Cd, Hg, As) although a number of them had background concentrations which exceeded Federal Guidelines for the protection of aquatic life.

Wet Mining

The water quality impacts arising from wet mining will depend on the water quality of the dredge pond, the mechanism of the outlet and it's location with respect to the regional drainage system. No direct studies of runoff water quality from wet mining operations have been conducted to date. However the Minnesota study (Brooks et al., 1982) reveals that the water quality of shallow dredged ponds in peatlands is significantly affected by the composition of the bottom substrate. In the study, two one-acre ponds were dredged in a fen area containing moderately decomposed reed-sedge peat, with an

average water depth of 1.6 m. One pond had a peat bottom, the other a clay bottom. Although large seasonal variations occurred in both ponds, water quality monitoring revealed significantly higher conductivity, alkalinity and major cation concentrations in the mineral pond. These were attributed to influence of the mineral substrate. Colour and acidity were higher in the peat pond. However pH showed little variation between ponds (7.6 in mineral pond, 7.2 in peat pond), indicating the groundwater influence in both ponds. Nutrient and heavy metal concentrations were not significantly different between ponds.

8.2.2 Enviromental Fate of Contaminants Released in Peat Mine Effluent

Once introduced into the aquatic system, the organic and inorganic consituents of effluent waters are acted upon by a complex array of physical, chemical and biological processes which may affect their ultimate impact on aquatic biota. General understanding of these processes permits estimations of ranges of bioavailable contaminant concentrations, provided that chemical properties and quantities of effluent are known.

Hydrodynamic and dilution processes are expected to be the most important physical processes controlling the fate of mine effluent constituents in open water environments. The relative importance of physical transport and dilution processes (downstream flow, turbulent flow and water currents) depends on the specific nature of the surface waters concerned (e.g., stream gradient, lake volume, discharge rate, etc.).

Other physical transport and transformation processes that may control the fate of peatland drainage consituents in watersheds are volatilization, sorption-desorption and settling and resuspension of particulates. Volatilization is the process whereby dissolved contaminants pass from water into the overlying atmosphere. This process may be important for high vapour pressure organics and inorganics such as many low molecular weight hydrocarbons, elemental mercury and hydrogen sulphide. Dissolved substances may react physically or chemically with other materials in the water column and become particulate in form. These particulates may then settle. Resuspension of particulates by increased water motion (e.g., waves, currents) may result in contaminant transport. Particulate contaminants may re-solubilize depending on water quality conditions. This could result in secondary re-contamination of the water column. Sorption-desorption

processes may be important in the dispersion of many metals and organic compounds. Loss of contaminants from the aqueous phase by volatilization, sorption and settling is generally perceived to reduce bioavailability and toxicity. However, removal of contaminants from the water column to the sediments may affect benthic populations, and thus indirectly affect their predators.

Among chemical transformation processes, acid neutralization reactions may be most important in determining the impacts of peatland drainage. The buffering capacity or alkalinity of receiving waters will determine their capacity to neutralize acids in peatland waters. In freshwaters, alkalinity is usually imparted by bicarbonates, carbonates and hydroxides; the CO_2-$H_2CO_3^*$-CO_3 equilibrium system is generally of primary importance in this regard. However, in low alkalinity waters, carbonate alkalinity may be close to zero, and much of the observed alkalinity is "residual" alkalinity due to substances behaving as weak acids (pK 4-6). Such substances include organic acids, iron and manganese oxides, clay minerals and ammonia. Waters from ombrotrophic peatlands have little alkalinity and may be quite acidic, while waters from minerotrophic peatlands have higher alkalinity and tend to be less acidic. Surface waters in much of Canada are poorly buffered and readily acidified, particularly in areas characterized by shallow, non-calcareous soils and insoluble igneous rocks which impart little alkalinity to runoff and grondwater (Harvey et al., 1981). Poorly buffered waters are susceptible to more extensive acidification by peatland drainage than are well-buffered systems.

Other chemical transformation processes in surface waters include photolysis, oxidation-reduction reactions and hydrolysis. Photolytic reactions may break down many organic and some organo-metallic compounds into simpler molecules. Oxidation-reduction reactions fragment compounds through the destruction of chemical bonds or form new compounds through bonding of reaction groups. Hydrolysis is an acid-base transformation resulting in the addition of a hydroxyl radical. Many organic compounds and multivalent inorganics undergo oxidation-reduction and hydrolysis reactions in surface water systems.

Bioaccumulation - the uptake of contaminants from the aquatic environment by organisms - can result in the accumulation of contaminants through food chain transport. Bioaccumulation also serves to remove contaminants from the water column through the settling of plant and animal remains to the sediments.

Biotransformation and biodegradation of contaminants alter the chemical structure (and toxicity) of contaminants. Organic compounds such as those comprising the DOM, prevalent in brown-water systems, are metabolized by organisms (primarily bacteria) into progressively simpler forms. Some compounds are metabolized rather quickly (e.g., degradation half-life of days) while others, such as various phenolic compounds found in humic acid complexes, are much more resistant to degradation (Wetzel, 1975). Inorganic compounds may also undergo biotransformation; for example, readily bioaccumulated methylmercury form.

2

Preliminary Model Development

9.0 MODELLING STUDIES

In the preceding sections, we have identified and described the behaviour of key physico-chemical and biological variables which define peatland ecosystems. In this section, we begin to quantify these processes through the development of a series of models. The framework for model development has been determined by the balance between two major considerations:

- to develop a model which is general enough to address the needs of a variety of multidisciplinary users; and
- to depict the complex peatland ecosystem in enough detail to allow accurate prediction of impacts.

The final version of the model will incorporate multi-disciplinary literature data, field studies and controlled laboratory experiments. This report includes only the preliminary stages of model development; an overall model framework is developed, conceptual models of major variables are described, and initial simulations are made. All input values and process pathways are based on information available from the literature.

Specifically, this report contains the following:

- a description of the model framework, including ultimate goals, major assumptions, rationale for choice of input parameters, and model limitations;
- development of preliminary hydrology model;
- conceptual models for pH, major cations, carbon, nutrients, heavy metals, oxygen and redox potential;
- analysis of water balance in an undisturbed bog and alterations produced by wet and dry mining;
- simulations of peat accumulation processes and electroneutrality balances (pH) in an undisturbed bog; and
- simulation of water chemistry of outflow from a bog subjected to dry mining. Parameters considered include pH, nutrients and metals and toxicity.

9.1 The Modelling Process

9.1.1 Limitations of Models

A model is an "abstraction of reality". It describes, in either qualitative or quantitative terms, a certain set of the complex interrelationships of the system being studied. Modelling at the ecosystem level of necessity involves a number of assumptions and limitations. These generally reflect uncertainties regarding the behaviour of individual variables, incomplete understanding of process pathways or the sheer complexity of the system. The uncertainties of ecosystem modelling are summarized by Osborne et al. (1982) in the following.

"At a technical level, the following dangers exist. The transport through the environment of many chemicals is not well known or can be predicted only with considerable uncertainty. The effect of possible management strategies on the long-term dispersal of wastes is not well known. The effects of chemicals upon humans is not precisely known although those for radionuclides are probably among the best documented. The understanding of long-term biogeochemical processes is not well known."

The quandary, then, is that contaminants from peat mining will exist and that reasonable and acceptable decisions concerning their long-term management have to be made in the face of this uncertainty.

The preliminary peatland models which have been developed provide a useful organizational framework for data collection and also highlight areas requiring further study. However, their predictive capabilities are currently limited by lack of field data and inadequate testing. The models described below represent models which have been constructed and partially calibrated. They are presented in an illustrative fashion for diagnostic purposes.

9.1.2 The Model Framework

Various frameworks for analyzing the capabilities of a predictive model have been developed. Snodgrass (1979) describes the framework in terms of a sequence of steps:

(i) **Understanding the System of Concern**

(ii) **Stating Modelling Objectives**

A model is constructed to address a set of specific objectives; for different objectives, a different model may need to be formulated.

(iii) **System Discretization**

System discretization involves breaking the system up physically into boxes and subdividing each box into compartments. These boxes and compartments are homogeneous and are the entities about which the model is constructed. For example, boxes considered in the peatland hydrology model are the hydrologically active zone (acrotelm), and the inactive zone (catotelm).

(iv) **Model Construction**

Model construction involves developing the conceptual model quantitatively (e.g., equations describing essential processes) and the necessary computer coding.

(v) **Model Calibration**

Model calibration is the selection of unknown coefficient values using laboratory, literature and field data.

(vi) **Model Verification**

(vii) **Model Prediction**

Model verification involves testing the model with sets of data independent from those used for model calibration. More modelling work may be required if the model fails its verification tests. The anticipated use of a model determines how many steps need to be completed and the extent of model testing. For uses which are of a diagnostic nature (e.g., assembling knowledge and defining the most important processes), model construction may be sufficient. Model calibration may be sufficient for scenario testing. But to make statements about absolute concentrations expected in receiving waters requires adequate model verification. Where multimillion dollar decisions are to be based upon a set of model predictions, extensive verification studies are usually required.

The extent of calibration and verification required for peatland modelling is a question of confidence - How much confidence does one desire to have in the results? How much uncertainty is one prepared to accept? Tests for verification studies involve several levels. The first level is "judgement"; the model must describe the peatland sensibly and include all essential biogeochemical processes. A second level compares model predictions with field observations of the undisturbed ecosystem. Visual observation has, in general, been an accepted method for assessing this comparison; future work will probably involve use of statistics to assess the comparison. A third level involves comparing model predictions with observations for a peatland as it is disturbed. A final level assumes that some uncertainty will remain, and attempts to quantify this uncertainty; these methods may involve Monte Carlo simulation (e.g., IEC BEAK, 1983) or first order error analysis.

9.1.3 Peatland Conditions Modelled

The model will ultimately be capable of simulating conditions in:

- an intact peatland,
- a peatland with vegetation removed,
- a peatland subjected to dry mining, and
- a peatland subjected to wet mining.

Modelling of an intact peatland is the reference condition. Agreement of model calculations with field observations would provide some confidence in using the model to extrapolate to disturbed conditions. Simulations of impacts concentrate on predictions of water quality and quantity in the bog outflow. These should consider conditions both during peat drainage and mining and after closeout.

9.2 Master Variables

A bog is essentially a system in which inputs of carbon (CO_2), nitrogen (ammonia or nitrate, or N_2 fixation), phosphorus, sulphur and water (H_2O) are fixed into a particulate phase (herein called peat matrix) by vegetational growth. Subsequent decay results in

release of these components to a soluble phase. From here, they may either be lost from the bog through atmospheric or aquatic pathways, may remain in the soluble phase, or may be transformed back to a particulate phase (e.g., as a metal precipitate or via adsorption).

Other elements such as metals also enter the bog through atmospheric pathways. They may be incorporated into the peat matrix through plant growth, complexed with soluble organic material (assumed here to be primarily 'fulvic acid'), adsorbed to the peat particulate phase, or precipitated (e.g., as a metal sulphide in anaerobic waters).

The reduced oxidation state is a fundamental property of bogs in their saturated zone. It is maintained by the decomposition of organic materials and the lack of oxygen transport. The decay process may be conceptually viewed as a series of oxidation-reduction reactions in which the partial oxidization of one material (i.e., carbon) provides energy which drives a reduction process (i.e., Fe (III) to Fe (II)). The final electron acceptor for the reaction may be oxygen, nitrate, sulphate or certain organic molecules (see Section 9.4). Reduction-oxidation potential (Eh or pE) can be calculated by identifying the redox reaction which maintains the degree of reduction.

The fulvic acid (FA) formed by decay appears to control the pH of most ombrotrophic bog waters (Section 5.2.1). Addition of more basic groundwaters containing inorganic carbonate can induce a higher pH.

The following are viewed as the master variables for the model:

- flow pathway and the rate of water flow,
- bog pH,
- redox potential (Eh or pE),
- bulk density and decay rate of peat,
- adsorption properties of peat,
- soluble organics, and
- chemical precipitates.

The flow pathway is controlled primarily by the organic structure of the peat and the hydraulic conductivity. pH and Eh are master variables, but are themselves controlled

respectively by buffering systems (e.g., FA, inorganic carbon) and biochemical reactions (e.g., 0_2-CO_2, NO_3^--NH_4^+, NO_3^--N_2, SO_4^{2-}-H_2S). The rate of decay, adsorption properties, and concentration of soluble organics are all functions of peat characteristics and biochemical reactions. Chemical precipitates describe the mass of metal in a reformed soluble form. They are also functions of pH and Eh. For example, FeS could form at a low Eh. FeOOH could form at a high Eh and modest pH. $FeCO_3$ would form at a low Eh and high carbonate concentrations (hence neutral pH).

9.3 Model Construction

A generic ombrotrophic peatland has been formulated. It uses, as a baseline, Hemond's (1980) study of Thoreau Bog, Massachusetts. This is one of the few complete mass balance studies for a peatland system.

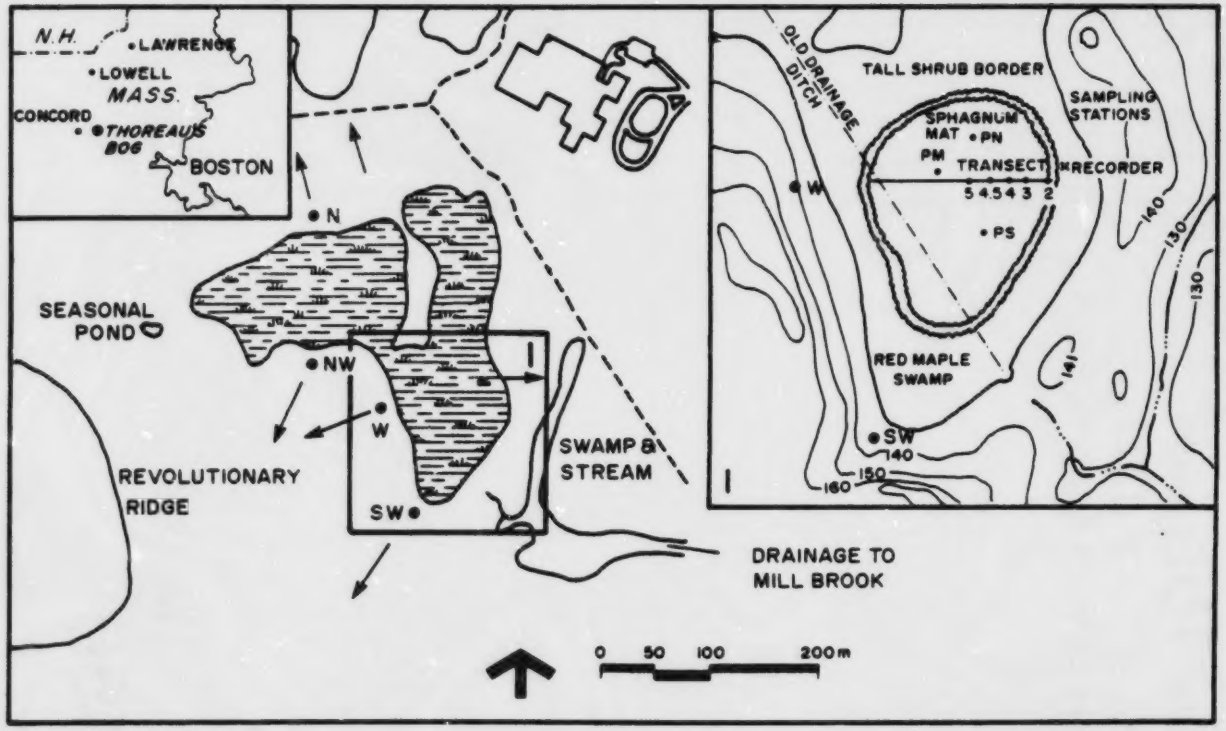
Physically, the generic bog has three distinct zones, referenced to 10 m at the edge of the bog and 10.5 m at the dome of the bog (see Figure 14). The reference plane (Z = 0) corresponds to the piezometric head of zero of the stage-discharge relationship (Figure 15a, b). There is a 30 cm thick zone of surface peat above the reference plane in which Sphagnum is assumed to grow. This zone is hydrologically the most active zone (acrotelm). Ten centimetres above the reference plane (i.e., at the bog stage = 10 cm, Figure 15b) is another plane which Hemond's data suggest represents the dividing line between 'subsurface runoff' and 'surface runoff'. 'Surface runoff' is assumed to represent horizontal flow through porous peat, as opposed to overland flow.

The second zone is the zone in which Hemond obtained depth examples for peat (bulk density and Pb-210 for dating) from which peat decay rate data can be calculated. This zone, 60 cm thick, was calculated to have accumulated over approximately 132 years and has the bulk density profile given in Table 21. All data are directly from Hemond (1980) except the age of the .36 to .48 m depth layer has been recalculated (see Section 9.5) as 95 years rather than the value of 71 years given by Hemond. The top 24 cm of Zone II is hydrologically active because of annual water table fluctuations.

The third zone of the 'generic' bog has similar anaerobic processes to those of the lower depths of Zone II and is hydrologically quite inactive on an annual time scale. This is a zone for which Hemond gives vertical data for magnesium, potassium and lead

FIGURE 14

Thoreau's Bog, Massachusetts (Hemond, 1980)



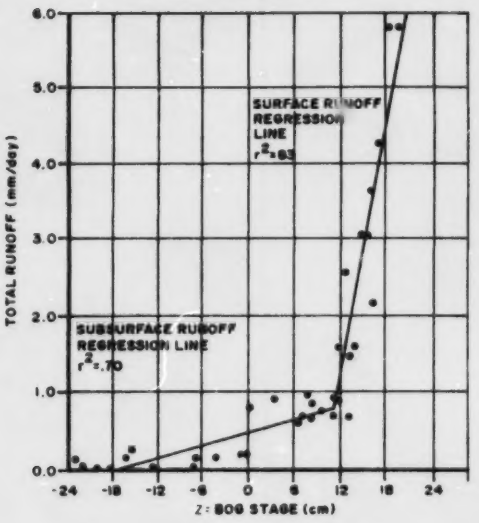
PIEZOMETER LOCATIONS ●

DIRECTION OF GROUNDWATER FLOW ⟶

PRECIPITATION COLLECTION STATIONS PM, PN, PS

FIGURE **15a**

Stage vs. Runoff Curve for Thoreau's Bog (Hemond, 1980)



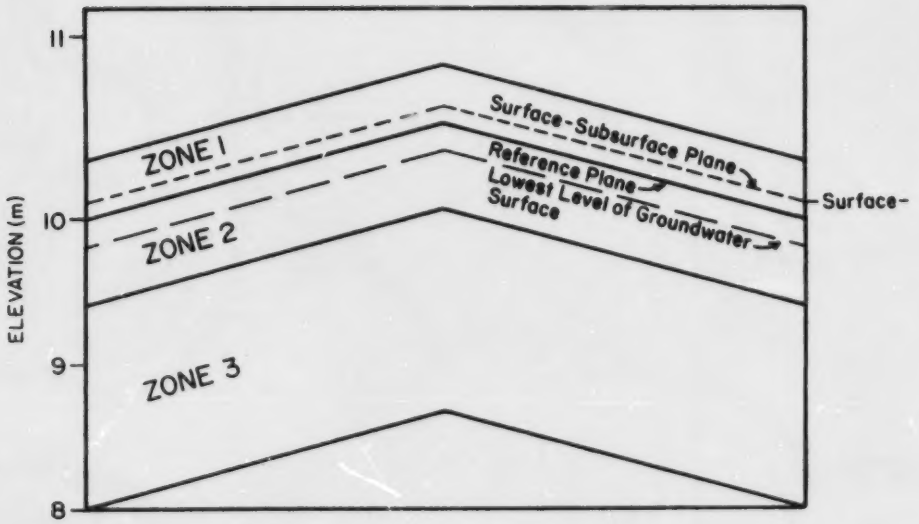


FIGURE **15b**

Hydrological Zones of Model Bog

TABLE 21: CHARACTERISTICS OF ZONE 2 FOR GENERIC PEATLAND

Depth (m)	Peat Bulk Density (kg/km^3)	Age at Bottom of Increment (gr)
0 - .12	24	6
.12 - .24	50	30
.24 - .36	43	58
.36 - .48	40	95
.48 - .60	44	132

concentrations and for magnesium distribution coefficients, but does not give bulk density data.

Below this third zone, it is assumed that there is an inactive support media which does not interact with the overlying zone. This inactive media may be older peat or other materials (e.g., sand). It is assumed to have a slightly higher hydraulic conductivity than that of the peat directly overlying it. This basement media in our generic bog differs from that of Thoreau's Bog which consists of water pools.

The chemical composition for the generic peatland is given in Table 22. The data are abstracted primarily from Tables 16, 17 and Figure 7 of this report, and from Gorham et al. (1984) and are consistent with Hemond's (1980) values for Mg, K and Pb, but may vary for SO_4^{2-}, NO_3^-, NH_4 and Cl^- (compared to the values of Table 22).

9.4 Hydrology

This section describes the water balance for the generic bog and compares model calculations of water levels to Hemond's (1980) field observations.

Water Balance

The water balance of Hemond (1980) for Thoreau's bog is given in Figure 16a. It assumes steady-state conditions, with no net change in storage and no vertical transport across the bottom boundary of the bog. The rainfall rate is typical of marine climates. Seventeen percent of annual precipitation is discharged as surface runoff, while 83% is lost via evapotranspiration. The long-term water balance may differ from these values somewhat because field observations are based upon only 15 months of data. However, review of the literature indicates that, as a general rule, in undisturbed bogs, greater than 60% of net annual precipitation input is commonly removed through evaporation (Table 2). Thus, for the generic peatland, it is assumed that there is no groundwater inflow and the water balance is represented as that expected for an ombrotrophic bog in a coastal region.

Hemond's (1980) assumption of no vertical transport across the bottom boundary of the bog should be checked. For the 'generic' bog model, vertical water transport has three

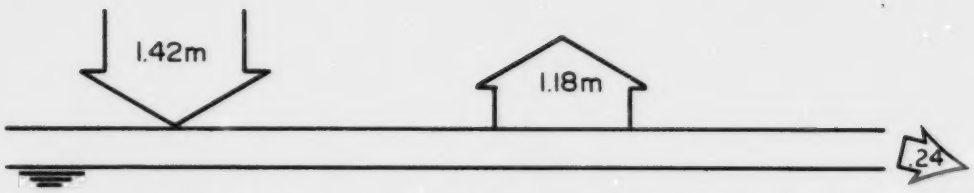
TABLE 22: CHEMICAL COMPOSITION OF SURFACE LAYERS OF ZONE 2 OF GENERIC PEATLAND

Element/Compound	Peat Concentration	Pore Water Concentration
Ca^{2+}	1.2 mg/g[1]	27 ueq/L[3]
Mg^{2+}	1.2 mg/g[1]	37 ueq/L[3]
K^{+}	0.4 mg/g[1]	5.2 ueq/L[3]
Na^{+}	0.2 mg/g[1]	96 ueq/L[3]
Al^{2+}	0.4 mg/g[1]	0.8 mg/L[4]
Fe^{2+}	0.8 mg/g[1]	1.4 mg/L[4]
Mn	7.0 ug/g[1]	0.05 mg/L[4]
Cu^{+}	10 ug/g[1]	0.04 mg/L[4]
Zn^{2+}	30 ug/g[1]	0.08 mg/L[4]
Hg^{2+}	.01 ug/g[1]	10 ug/L[4]
Pb^{2+}	25 ug/g[1]	0.05 mg/L[4]
H^{+}	5 mg/g[5]	$10^{-3.5}$ M[1]
CO_3^{2-}	400 mg/g[2]	10^{-5} M[2]
NH_3	10 mgN/g[1]	0.4 mgN/L
PO_4^{3-}	0.3 mg/g[1]	0.1 mgP/L
S^{2-}	1 mg/g[5]	0.01 mg/L[6]
Cl^{-}	-	100 ueq/L[1]
Br^{-}	-	-
AsO_4^{3-}	1 ug/g[1]	2 mg/L
$H_2SiO_4^{2-}$	-	2 mgSi/L
$B(OH)_4^{-}$	-	-
SO_4^{2-}	-	18 ueq/L[1]
NO_3^{-}	-	0.06 mg/L[2]
FA^{-}	-	29 mg/L DOC[1]

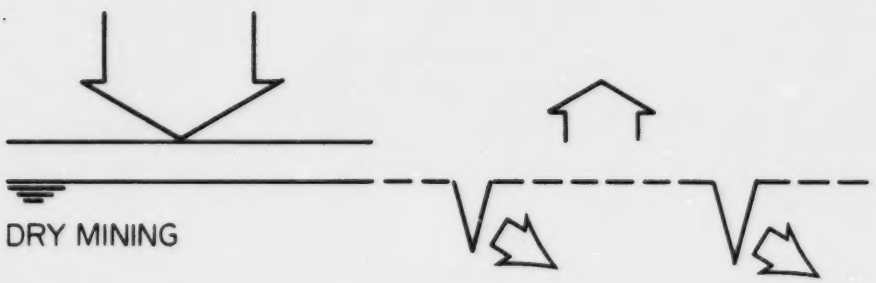
[1]Abstracted from Table 17, Figure 7
[2]Peat is 50% carbon by weight; pore water is at equilibrium with the atmosphere
[3]Gorham et al., 1984
[4]Abstracted from Table 18
[5]Table 16a
[6]Assumed

FIGURE 16

Water Balance



A. UNDISTURBED BOG (HEMOND, 1980)



B. DRY MINING



C. WET MINING

different components. A vertical component occurs due to bog formation and consolidation (squeezing). Rainfall raises the level of this component; runoff (horizontally) lowers it. Vertical piezometric gradients cause flow across the bottom. Provided that vertical piezometric gradients are locally downward, groundwater would always tend to move vertically downward. The actual vertical transport rate will depend upon the magnitude of the gradient and the vertical permeability of the peat.

Thus, vertical gradients may be calculated as follows. If a frame of reference is adopted at the peat surface, pore water has a downward velocity with respect to the frame of reference because the peat surface is rising due to peat accumulation. This velocity (5 mm/year in Hemond's study) is of the same order or higher than post-glacial rebound in the Great Lakes Basin (1 cm/100 years in Toronto; 5-10 cm/100 years on the North Shore of the Upper Great Lakes). It is quite small compared to rainfall (1.42 m/yr) and runoff (0.24 m/yr) in Hemond's study. Likewise, consolidation processes produce a similar relative downward velocity.

Vertical permeability may be estimated from the following example. Consider vertical gradients for fractured sandstones in northern Saskatchewan in which the vertical permeability coefficient is 2×10^{-5} cm/sec across a 100 m strata and the vertical gradient is 1%. A net infiltration rate of a 7 cm/yr was calculated using a finite element model (BEAK, 1980b). This provides a reference point for critiquing peatlands. Boelter's relationship (Figure 7b) suggests that a hydraulic conductivity coefficient of approximately 2×10^{-5} cm/s is expected in peat with a bulk density of 0.2 g/cm^3. For Hemond's data (0.025-0.04 g/cm^3 at the top of the bog), Boelter's relationship suggests that the hydraulic conductivity would be two orders of magnitude larger. Assuming that the bottom of the bog has a vertical hydraulic conductivity coefficient of the order of 2×10^{-5} cm/s, one can expect a vertical downward flow out of the bog of 0.7 to 7 cm/yr depending upon whether the vertical piezometric gradient is 0.1% or 1% respectively. Thus, flow rates may vary from negligible to significant in comparison with surface runoff (e.g., .24 m/yr in Hemond's case).

These calculations suggest that field measurements of vertical permeability coefficients as well as vertical piezometric gradient should be made for future model calibration.

Evaporation from a bare sandy loam soil removes on the order of 50% of net precipitation input, in continental climatic regions. Using this value and those for undisturbed bogs as reference points, it is conservatively estimated that vegetation removal and peat drainage will reduce net evaporative water removal to less than 50% of net precipitation input, with the remainder being lost via runoff (see Figure 16b - Dry Mining).

For wet mining, the relative proportion of evaporation to runoff is expected to be similar to the undisturbed state (see Figure 16c - Wet Mining). For the lower Great Lakes, hydrologists use the rule of thumb that annual evaporation approximately equals direct rainfall. Some variations occur from water body to water body depending upon annual rainfall and variations in factors affecting evaporation (wind speed, relative humidity, air temperature, atmospheric and solar radiation). For marine climates, evaporation from a water surface does not routinely equal rainfall because rainfall rates are higher and evaporation rates may be lower than continental climates.

Water Levels and Storage Time

Aanalyses of the bog stage-discharge relationship, and simulation of water levels at the outlet are derived for the generic peatland using Hemond's (1980) data. The stage-discharge relationship permits estimates of hydraulic conductivity:

$$\text{slope} = \frac{\text{change in runoff rate}}{\text{change in height of water}}$$

For Section 1 of the stage-discharge curve (Figure 15a), the vertical runoff rate increases approximately 0.8 mm/d for a 0.28 m rise in water table level. Assuming that the effective area contributing to runoff is 40 m x 100 m (Figure 14a), this produces a horizontal velocity of 4.1 cm/d per 0.28 m rise in height. For Section 2, the vertical runoff rate increases 6 mm/d for a 0.1 m rise in the water table, or a horizontal velocity of 0.9 m/d per 0.1 rise. Using Boelter's relationship between hydraulic conductivity and bulk density, the hydraulic conductivity is 0.01 cm/s for the first layer (0.024 g/cc). Using Darcy's equation, $Q = -K \Delta H/l$ (Section 4.4), the slope of the groundwater gradient in the first layer would be of the order of 0.5%.

Hemond (1980) does not give bulk densities for the second layer. Assuming the same characteristics as the first layer, the slope of the groundwater gradient would be 10%. This is clearly not possible, given the apparent slopes of Thoreau's bog (Figure 14). Hence, the bulk density and hydraulic conductivity of the second layer must be different from that of the first layers. Assuming a hydraulic gradient of 0.5%, the conductivity coefficient would be of the order of 0.2 cm/s for the second layer. Boelter's relationship would suggest a bulk density on the order of 0.005 g/cc.

These calculations provide reference data for calibrating the hydrology model for the generic peatland and illustrate how similar approaches could be used for other peatlands. In the near future, contact will be made with Dr. Hemond to see how well these calculations agree with other physical data.

The monthly height of the water table in Thoreau's bog has been simulated using the dynamic water balance equation:

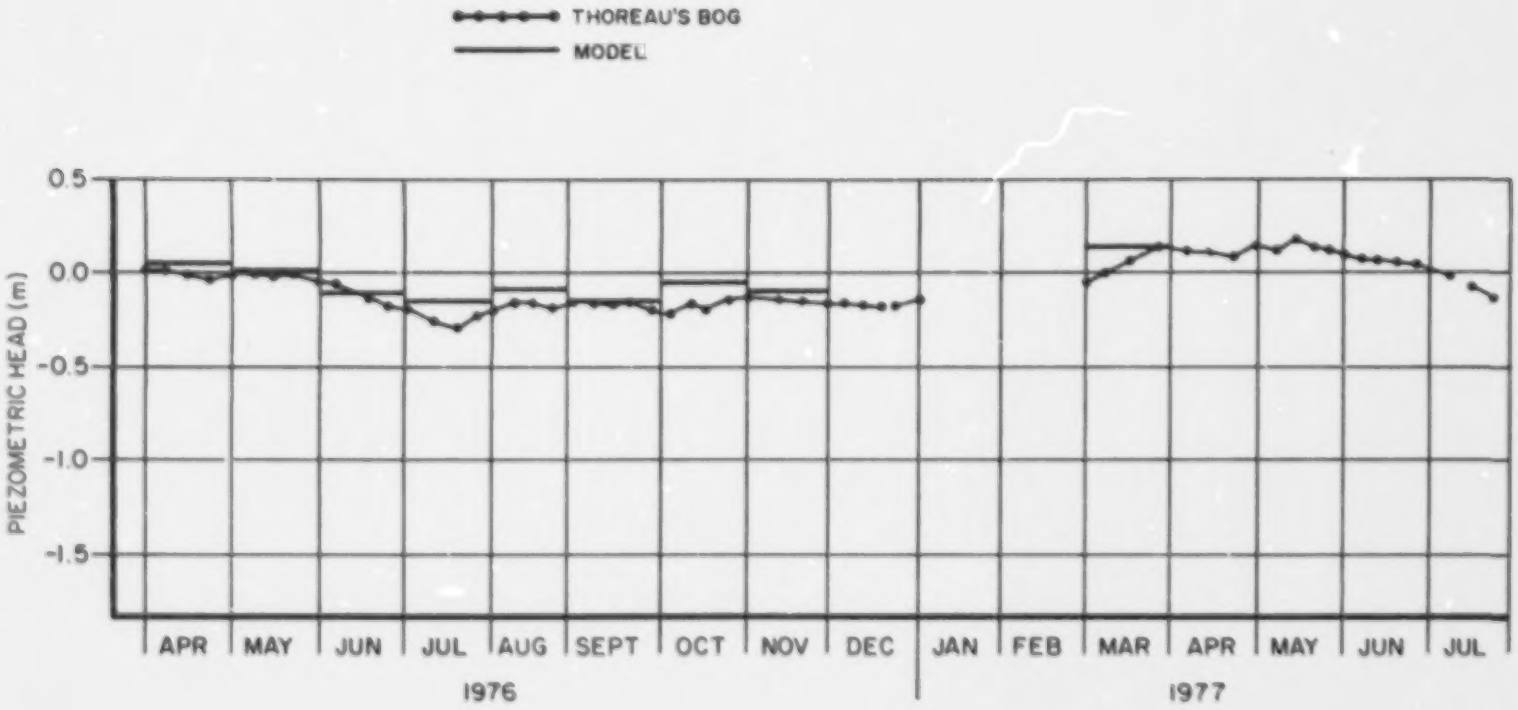
$$\Delta S = P - E - D \quad \text{(Section 2.0)}$$

The results are given in Figure 17. Overall, there is reasonable agreement between observed and predicted levels. There is some discrepancy between observations and calculations in mid-summer and in late fall. This results particularly because evapotranspiration dominates losses from the bog.

Some simulations have also been made of the dynamic changes in water table elevations across bog layers assuming the hydraulic conductivity coefficients given above for layer 1 and layer 2. These are not presented since the order of magnitude change in hydraulic conductivity coefficient which has been assumed to occur at the boundary between the two layers is not physically realistic. They do suggest, however, that a timing constant of the order of a month for runoff is reasonable.

The simulation of the water table height also allows some comments concerning the effect of storage upon runoff. The change in storage in summer is typically on the order of 0.05-0.1 m/month. Compared to the annual rainfall, this change is small (4-8%), but compared to annual runoff, it is substantial (20-40%). As previously mentioned (Section 2.0), some literature suggests that bogs can store large amounts of rainfall and influence

FIGURE 17 Water Table Levels in Thoreau's Bog and Model Calculations



runoff for perhaps a year. Both the model simulations and Hemond's data suggest that spring storage influences runoff for only two to three months, after which runoff may cease (July, August). This suggests that the bog may act as a temporary buffer for runoff for a couple of months, but not for annual time scales.

9.5 Conceptual Models for Chemical Parameters in the Bog

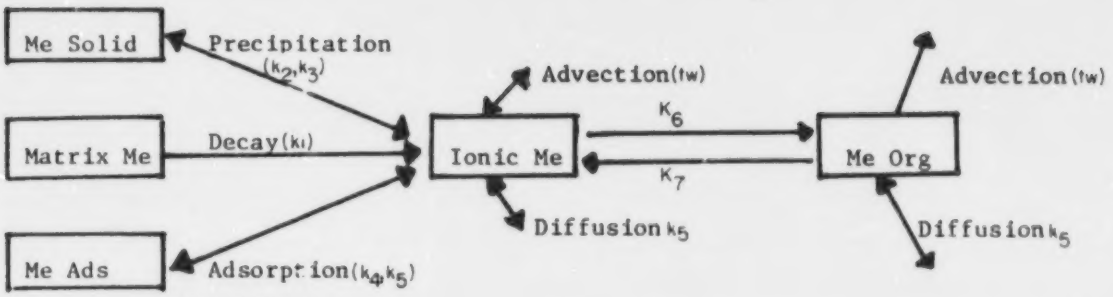
This section presents a conceptual set of models which describe transformations governing changes of chemical state between particulate and soluble forms of the chemical parameters shown in Table 22. The development of these models allows one to evaluate concentrations of parameters in the outflow for different peat harvesting options (e.g., dry and wet mining). The parameters of concern are:

(i) pH
(ii) Representative major elements (Ca^{2+})
(iii) DOC
(iv) Nutrients (NH_3, NO_3^-, TP)
(v) Heavy Metals (Fe, Al, Cu, Mn, Hq, As)
(vii) Potential toxicity factors (trace metals such as Cu)

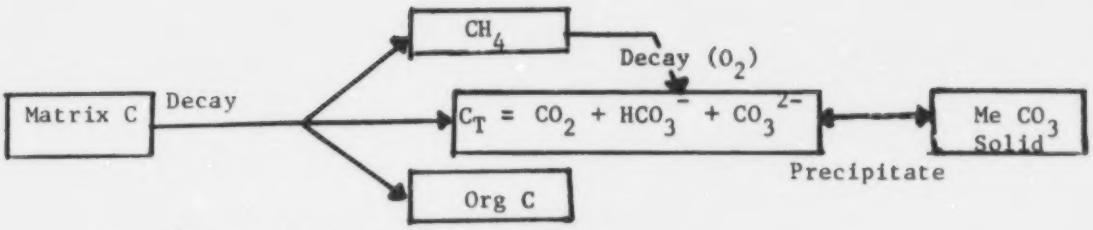
The modelling analyses begin with the biogeochemical processes within the bog since the bog is the source of potential contaminants. Figure 18 shows definitional sketches for metals (Figure 18a), carbon (Figure 18b), sulphur (Figure 18c), nitrogen (Figure 18d) and phosphorus (Figure 18e). Geochemical transformations are indicated. Transport along hydrological pathways is not indicated in the diagrams, except for metals, but transport processes are included in the mathematical models. In the models, solid phases are considered not to move whereas liquid phases (ionic metal, organic metal) are transported via advection (ADV) and diffusion (DIFF). In reality, solid phases move to a small degree due to consolidation or erosion (Imboden, 1975).

The definitional sketches show processes expected in anaerobic and/or pore waters of the peatland. They ignore the effects of Sphagnum growth (incorporation of CO_2, NH_3/NO_3, PO_4 etc., into fibre). Hence, the initial forms of the substances in the peat before mining, and processes effecting transformation from solid to solution phases, are the main questions considered.

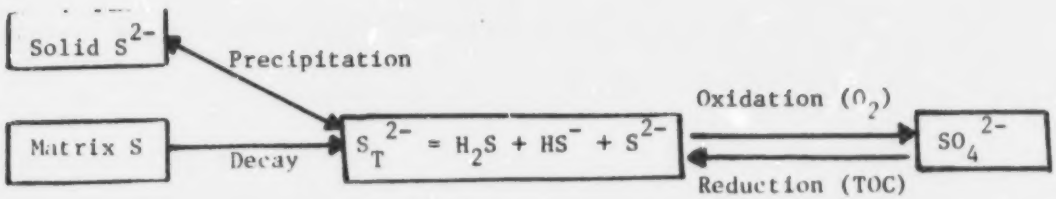
FIGURE 18 CONCEPTUAL MODELS



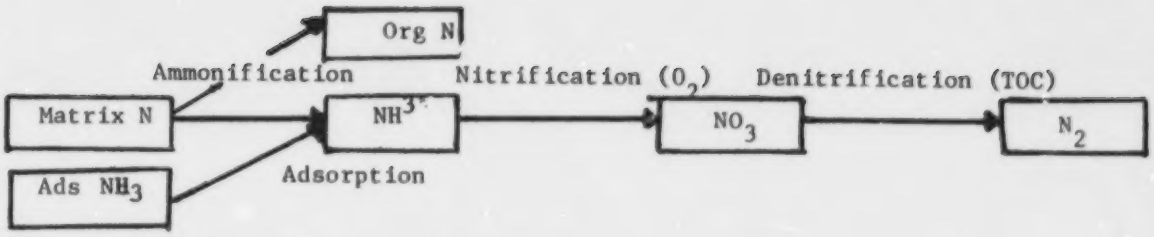
a Metals



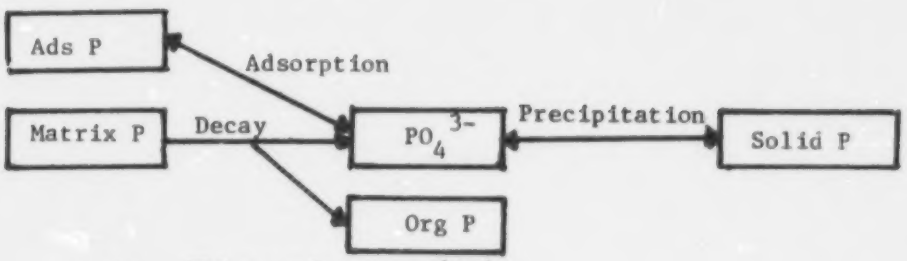
b. Carbon (C)



c. Sulphur (S)



d. Nitrogen (N)



e. Phosphorus (P)

9.5.1 Conceptual Model for Metals

A generalized equation describing the influence of all reactions in Figure 18a upon metal concentration in pore water is:

$$\frac{d[Me]}{dt} = \underbrace{k_1[MeF] - k_2[Me][Sol] + k_3[MeSol]}_{\text{Precipitation}} \qquad (1)$$

$$- \underbrace{k_4[Me]\left[\Gamma_m - \Gamma\right] + k_5\Gamma}_{\text{Adsorption}} \qquad \underbrace{\frac{1}{tw}\left([Me]_o - [Me]\right)}_{\text{Advection}}$$

$$+ \underbrace{\frac{k_s}{z_1}\left([Me]_u - [Me]\right) + \frac{k_s}{z_2}\left([Me]_d - [Me]\right)}_{\text{Diffusion}}$$

$$- \underbrace{k_6[Me][Org] + k_7[MeOrg]}_{\text{Metal Organic Reactions}}$$

Here

Me	is ionic metal
MeF	is metal content of remaining peat fibre and mosses
Sol	is the anion found in the precipitate, MeSol
MeSol	is the precipitate
Γ_m	is the maximum adsorption capacity (Cation Exchange Capacity for Me)
Γ	is the actual amount of metal adsorbed
Org	is the humic substance
MeOrg	is the metal-humic complex
[ ]	represents concentration
k_i	are reaction constants
tw	is the hydraulic residence time of the box
ks	is the mass transfer coefficient (a function of diffusion coefficient)
u,d	subscripts, representing upgradient and downgradient respectively

This equation describes all transformations in Figure 18a. It can describe any metal given in Table 21. It assumes that all reactions are kinetically controlled. However, it is too complex for our purposes. While many of the coefficients are available in reference books, others are unknown. Accordingly, simplifications have been sought. If it is assumed that chemical equilibrium exists in the box, equation (1) simplifies to the following.

$$[Me] = K_{so} / [Sol] \quad (2)$$

$$= \frac{m\,[Me]}{K_{me} + [Me]} \quad (3)$$

$$[MeOrg] = K_C \; Me \; Org \quad (4)$$

$$\text{Net Mass Transport} = \frac{1}{tw}\left([Me]_o - [Me]\right) + \frac{k_s}{z_1}\left([Me]_u - [Me]\right) + \frac{k_s}{z_2}\left([Me]_d - [Me]\right) \quad (5)$$

$$\text{Rate of Change in Mass of Me in Precipitate} + \text{Net Mass Transport} = k_1\,[MeF] \quad (6)$$

Here, K_{so} is the solubility product for MeSol
K_{me} is the adsorption constant
K_C is the complexation constant

This simplification is plausible and justifiable. But it presents several difficulties:

(i) not all metals are at equilibrium for time scales of concern,

(ii) some metals, do not form precipitates because their concentrations are less than the solubility limit,

(iii) for some metals, equilibrium can be used to model one reaction while kinetics can be used for other reactions.

Accordingly, a further simplification can be made such that only mechanisms known to be important are included in the conceptual model for any metal. This devolves into a metal by metal specific approach. The equations are based upon equilibrium or kinetic

considerations. The mechanisms considered to be important for individual metals are described below and summarized in Table 23.

Metal Adsorption

It is assumed that only Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} adsorb in significant amounts; the adsorption of these metals is typically described using cation exchange capacity concepts. Their adsorption could also be described by the Languir adsorption model. Other metals will adsorb; the linear distribution coefficient is typically used for such metals (O'Connor and Connelly, 1980). The Languir model becomes the linear distribution coefficient at low metal concentrations. For this report, it is assumed that adsorption of the other metals of Table 22 is negligible compared to other mechanisms.

Metal - Humic Substance Associations

It is assumed that univalent metals do not form organic complexes (e.g., Na^{+} with fulvic acid) in significant amounts, and that divalent metals form complexes which are at equilibrium with organic carbon during time scales of concern to peat mining. Trivalent metals are assumed to form complexes whose dissociation rate is kinetically controlled.

The association of metals with soluble humic substances is a "black box" in many respects. The structure of the organic molecule is often unclear. Complexation reactions with metals may change the structure and activity of reactive groups, and may even induce precipitation of the humic molecule (Schnitzer and Khan, 1978). Complexation involving one bond between a carboxyl group and a divalent metal may be followed by formation of a second bond; this changes the dissociation kinetics of the metal - organic molecule.

The relevant question to this study is whether a metal complexes with humic matter and whether equilibrium or kinetic considerations best describe the interaction. The assumption that univalent metals do not complex significantly is justified by the observation that Na^{+} and K^{+} are fully dissociated in laboratory solutions of standard complexing agents (e.g., EDTA). That humic substances form metal complexes with di-or trivalent metals is beyond dispute (e.g., Sedlacek et al., 1983; Dempsey and O'Melia, 1983; Luoma and Davis, 1983). In laboratory solutions, metal humic complexes form

TABLE 23: MECHANISMS USED FOR METALS

Metal	Adsorption		Organic Complexation		Precipitation	
	Equilibrium	Kinetic	Equilibrium	Kinetic	Equilibrium	Kinetic
Ca^{2+}	ALL		ALL			
Mg^{2+}	ALL		ALL			
K^{+}	ALL					
Na^{+}	ALL					
Al^{3+}	N		IC	MIN	I	
Fe^{2+}	N		IC	MIN	IC, S, I	MIN
Mn^{2+}	N		ALL		IC, S	MIN
Cu^{2+}	N		ALL		IC, S	MIN
Zn^{2+}	N		ALL		IC, S	MIN
Hg^{2+}	N		ALL		IC, S	MIN
Pb^{2+}	N		ALL		IC, S	MIN

ALL - important before and during peatland development

IC - important before peat mining

MIN - important during and after mining

S - sulphide precipitate

N - not clear. Mechanism should exist for all metals and be described by a linear distribution coefficient. It is assumed for these metals that adsorption is negligible compared to the magnitude of the other mechanisms.

I - hydroxide precipitation mechanism will become important as pH increases

Note:

Mechanisms assumed are for an ombrotrophic bog with a pH of 3-4. The mechanisms may become important as environmental conditions change. For example, if the pH increases, hydroxide precipitate formation becomes important for aluminum in the pH 4.5 - 5.5 range. If the redox conditions change from anoxic to aerobic, iron sulfide will oxidize to form soluble iron, but the iron may reprecipitate as iron hydroxide.

rapidly. What is unclear is the nature and strength of the bonding and the kinetic rate of dissociation.

Driscoll et al.'s (1982) data for aluminum provide a reference point for trivalent metals. They estimated concentrations of monomeric, Al-F, organic-Al and solid forms of aluminum through a small New Hampshire watershed subject to acid rain. Aquatic environments measured included small streams, flowing into larger streams to a lake. If equilibrium existed from headwaters through the lake system, an equilibrium constant defined by,

$$K_C = \frac{[Al\ Org]}{[Al]\ [Org]} \qquad (4A)$$

would describe the observed data.

Our analyses of their data indicate that K_C is not constant: In fact, organic aluminum becomes several orders of magnitude out of equilibrium with the observed concentrations of Al^{3+}. Furthermore, the ratio of organic Al^{3+} to TOC is approximately constant. This suggests that dissociation kinetics for organic Al^{3+} have a half-time which is much longer than one month in acidic systems (the travel time through Driscolls's sytem), and hence, that kinetics would control the dissociation rate for organic aluminum from peat leachate.

Data for divalent metals which is as unambiguous as Driscoll's data for aluminum have not been found. Some data sets give complexation constants (Luoma and Davis, 1983). Others permit some observations, but have not been fully critiqued. For this report, the effect of dissociation kinetics of organic divalent metals is tested using a sensitivity analysis.

Metal Precipitates

Metal sulphides are assumed to be the dominant forms of metal precipitates in anoxic zones of the generic bog. Of plausible metal forms (sulphides, carbonates, hydroxides, sulphates), sulphides are generally the thermodynamically most stable. Exceptions include iron (II) carbonates which can form in environments where aqueous

concentrations of carbonate are sufficiently high (e.g., Morin, 1983). However, ombrotrophic bogs generally contain little carbonate. The key questions are whether aqueous sulphide is present and whether aqueous concentrations of metals and sulphide are high enough to cause precipitation.

Clymo (1983) presents two sets of data which indicate the probability of metal sulphide formation. In one Sphagnum fuscum peat bog (Andoya, Norway), traces of sulphide were detected a few centimetres below the water table, while strong traces were detected within 10 cm. In another study total metal concentrations were used to estimate the formation of metal sulphides. The analysis indicated that MnS was not expected to form while FeS, CdS and ZnS formation were expected; PbS and especially CuS and HgS had even higher formation potential. Other studies show that black lenses of material exist in peat cores; these lens are probably a metal sulphide solid.

Other inorganic particulates which may be present in peatlands are those derived from atmospheric dust, and chemical precipitates formed in adjacent mineral soils - bogs located near mine-mill complexes receive various particulates from stack emissions. Particulate lead probably enters the bog as a Pb-Br nuclei; whether it remains in this form or is converted to a lead sulphide or a lead organic compound is unclear. In minerotrophic peatlands, metal carbonates can form; trace metals which enter a fen through acidic rainfall could precipitate when the rainfall mixes with more alkaline groundwaters. For the preliminary models presented in this report, it is assumed that none of these forms are significant in the generic bog.

9.5.2 Conceptual Model for Carbon

The decay of particulate carbon in peat and its conversion to soluble forms of humic substances (labelled as organic carbon (DOC) in Figure 18b), inorganic carbon (C_T), ($= CO_2 + HCO_3^- + CO_3^{2-}$), and methane is the 'engine' which drives most of the processes of concern in an ombrotrophic bog. For any point in the bog, decay may be described as:

$$\frac{d\,[POC]}{dt} = -k\,[POC] \qquad (7)$$

First order kinetics have been widely used to describe decay rates (k) in bogs; values for k range from 10^{-2} to 10^{-5} yr^{-1} with typical ranges for bogs formed over a millenia quoted as 10^{-3} to 10^{-5} yr^{-1} (Section 3.3.3).

The mechanisms involved in the formation of methane, carbon dioxide and humic substances from the decay of POC are unclear. For anaerobic digestion theory, a two step process has historically been used to describe methane formation under anaerobic conditions - the conversion of particulate matter to a series of simple organic acids and then the coversion of these organic acids to methane and carbon dioxide. Such steps usually result in digestor gas containing 30% carbon dioxide and 70% methane. A more involved series of steps are being defined by the result of recent microbial work, particularly as it relates to anaerobic processes in marine sediments.

How fulvic and other humic substances form is not well understood. When viewed as a condensation product (i.e., due to aggregation of simpler molecules), decay of POC to produce soluble organic acids and other organic molecules provides source material for the formation of soluble humic substances. Alternatively, soluble humic substances could result from bacterially or mechanically induced cleavage of the molecules from POC. This would represent a decay-type process, but would proceed by a different mechanism than the one involved in methane formation. However, whether methane itself forms in solution or on the surface of POC particles is unclear. Given the affinity of bacteria for surfaces, methane formation at or near the surface of POC particles (i.e., on the surface of peat) would be most plausible explanation.

For the purpose of model development, it is assumed that fixed portions of POC decay to CH_4, CO_2, and humic substances in anaerobic pore waters. These portions will be calibrated at a later date using field data.

Decay rates change as a function of degradability of the plant material which forms the peat, pH, and redox condition. In this work, degradability is taken as a constant for a particular vegetation type (i.e., Sphagnum). Aerobic and anaerobic rates differ as a function of the ability of bacteria and yeast etc., to break down the peat. It is assumed that anaerobic rates are 0.5 times aerobic rates. The effect of pH upon decay rates is addressed in section 9.5.6.

The degree of humification is another method commonly used to assess the state of peat decomposition (see Figure 7). Humification (VP = von Post scale number, 0-10) can be modelled using the following empirical relationship (Clymo, 1983):

$$VP = 100 \quad (\text{Bulk density}) \tag{8}$$

9.5.3 Conceptual Model for Sulphur

Sulphur exists in a reduced state (S^{2-}) in peat. Peat decay liberates S^{2-} into solution as sulphide and other soluble organic S forms (Figure 18c); these latter forms are neglected herein. S^{2-} may precipitate with metals, in anaerobic waters, or is transported out of the anaerobic zone. Upon entering aerobic waters, sulphide may be oxidized to sulphate by sulphur-oxidizing bacteria. Sulphate from aerobic waters may be transported to anaerobic waters where it is reduced to sulphide. In the sulphate reduction reaction, sulphate acts as a final electron receptor, and organic matter as the energy source for sulphate-reducing bacteria.

In some bogs, substantial sulphate concentrations are found deep in the anaerobic zones. This suggests that sulphate reduction has ceased. This would occur if sulphate-reducing bacteria were inhibited or if there was insufficient organic carbon present to provide an energy source for bacterial growth. Recent microbiological work on sulphate reduction in estuaries suggests that a lack of specific organic carbon molecules, limits sulphate reduction reactions.

In the model, decay of matrix-S is assumed to be a first order reaction operating at the same rate as that of POC. Sulphide is assumed to be stable in anaerobic waters, except if participating in chemical precipitation reactions with appropriate metals. Both sulphide and sulphate are assumed to diffuse across the aerobic-anaerobic interface. Sulphide oxidization to sulphate is described by zero order kinetics (r_S; g/m^3-d). Sulphate reduction is described by zero order kinetics (r_{SO_4}; g/m^3-d). Both r_S and r_{SO_4} are calibration parameters which will be estimated from field/laboratory data. Because the cause of cessation of sulphate reduction in deep waters of certain ombrotrophic bogs is unclear, this limitation is treated mathematically as $r_{SO_4}=0$ for such waters. This limits, to some degree, the predictive capability of the model.

Complexation reactions involving H^+ with S^{2-} are quite rapid and may be described using equilibrium considerations with first and second acidity constants of $pK_1 = 7.0$ and $pK_2 = 13.0$ (Stumm and Morgan, 1981).

9.5.4 Conceptual Model for Nitrogen

The definitional sketch for nitrogen in anaerobic waters (Figure 18d) is similar to that for carbon, except that ammonia adsorption can occur. A linear distribution coefficient of 1-2, observed for neutral pH in highly organic sediments, is adopted here. The decay of particulate-N and its rate is modelled similarly to carbon. The decay product is unclear. Both ammonia and nitrogen are observed in pore waters. Ammonia can form from particulate organic nitrogen (PON) by hydrolysis of amine type groups (ammonification). The model assumes that a fraction of PON decay becomes soluble organic-N and the remainder, ammonia. The value of the 'fraction' is a calibration parameter.

Nitrification (r_N) and denitrification (r_{DN}) are modelled using zero order kinetics (g/m^3-d) and treated as calibration parameters. Nitrification occurs in two steps: ammonia to nitrite (by nitrosomonos) and nitrite to nitrate (by nitrobacter) (Section 5.3.1). Measurements for Hamilton Harbour sediments (pH 7.8) provide a reference for model calibration (r_N = 230 g N/m^3-d; r_{DN} = 43-86 g N/m^3-d, measured at 20°C); calibration of r_N for Quirke Lake (Halbert et al., 1980) provides a second reference point. The effects of pH and oxygen upon r_N are given below in Sections 9.5.6 and 9.5.7.

9.5.5 Conceptual Model for Phosphorus

The definitional sketch for phosphorus is shown in Figure 18e. The decay of matrix P is modelled similarly to that for carbon, and assumes that phosphorus and carbon are present in similar compounds. The model assumes that a fraction of matrix-P decays to PO_4^{3-} and the remainder to Org-P. Solid-P could precipitate as $CaHPO_4$ or iron phosphate, but here we assume that these forms are insignificant, relative to adsorption. Adsorption of P is described by a linear distribution coefficient.

9.5.6 Conceptual Model for pH

The pH of most aqueous systems is controlled by chemical electroneutrality (i.e., charge balance) and the concentration of total inorganic carbon (C_T) present. For many fresh waters, Na^+, K^+, Ca^{2+}, Mg^{2+}, C_T, SO_4^{2-}, Cl^-, H^+ and OH^- are the main ions which contribute to electroneutrality:

$$[Na^+] + [K^+] + 2[Mg^{2+}] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + 2[SO_4^{2-}] + [Cl^-] + [OH^-] \quad (9A)$$

When expressed with respect to the first equivalence point of the $H_2CO_3^*$ system, the equation becomes:

$$[Na^+] + [K^+] + 2[Mg^{2+}] + 2[Ca^{2+}] - 2[SO_4^{2-}] - [Cl^-] = C_C - C_A = \text{Alkalinity} = [HCO_3^-] + 2[CO_3^{2-}] + [H^+] \quad (9B)$$

Here C_C = net cation charge and C_A = net anion charge.

Alkalinity is a measure of the buffering capacity of the water. It represents the amount of acid which will be adsorbed by the water to reach the first equivalence point of H_2CO_3 (i.e., $[H^+] = [HCO_3^-]$). This is differentiated from the buffering capacity of the water at its <u>in situ</u> pH which is a measure of the ability of the water to resist a change in pH if a unit amount of acid is added. Thus, alkalinity (Equation 9B) is a statement of electroneutrality, expressed with respect to the first equivalence point of $H_2CO_3^*$ rather than the equivalence point analogous to the titration of a strong base with strong acid (Equation 9A).

Inorganic carbon (C_T) is composed of three species $H_2CO_3^*$, HCO_3^- and CO_3^{2-}. They are related by the chemical reaction,

$$H_2CO_3^* \rightleftharpoons H^+ + HCO_3^- \quad pK_1 = 6.3 \quad (10A)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \quad pK_2 = 10.3 \quad (10B)$$

Because the half times of these reactions are of the order of milliseconds, they can be considered to be at equilibrium. If C_T and pH are known, one can calculate the actual concentration of $H_2CO_3^*$, HCO_3^- and CO_3^{2-} defined by pK_1 and pK_2.

pH can be calculated from alkalinity and C_T because the concentration of H^+, HCO_3^- and CO_3^{2-} is fixed by the values of pK_1, pK_2. If the pH lies between 5 and 8 and the bicarbonate system is the main buffering system, the model for pH is,

$$\left[H^+\right] = K_1 \frac{C_T}{Alk} - 1 \tag{11A}$$

$$pH = -\log\left[H^+\right] \tag{11B}$$

This model is expected to be generally valid for most minerotrophic peatlands. However, it is inadequate for most ombrotrophic bogs because, humic substances (e.g., fulvic acid; FA) contribute significantly to electroneutrality through the complexation reaction,

$$HFA \rightleftharpoons H^+ + FA^-$$

Including this reaction, the electroneutrality condition in Equation (9A) is re-expressed as:

$$\left[Na^+\right]+\left[K^+\right]+ 2\left[Mg^{2+}\right]+ 2\left[Ca^{2+}\right]+\left[H^+\right]=\left[HCO_3^-\right]+ 2\left[CO_3^{2-}\right]+ 2\left[SO_4^{2-}\right]+\left[Cl^-\right]+\left[OH^-\right]+\left[FA^-\right] \tag{12A}$$

For this definition, one has the dilema of how to define alkalinity. One could define it such that all strong acids and strong bases are on the left hand side of the expression:

$$\text{Alkalinity} = \left[HCO_3^-\right] + 2\left[CO_3^{2-}\right] + \left[FA^-\right] + \left[OH^-\right] - \left[H^+\right] \tag{12B}$$

Equation 12B is the proper approach if one uses the rule that all species which contribution substantially to buffering intensity should be on the right side of the "alkalinity expression".

Alternatively, one could define alkalinity by the right hand side of Equation 9B and incorporate FA^- into the left hand side:

$$[Na^+]+[K^+]+2[Mg^{2+}]+2[Ca^{2+}]-2[SO_4^{2-}]-[Cl^-]-[FA^-]=\text{Alkalinity}=[HCO_3^-]+2[CO_3^{2-}]+[OH^-]-[H^+] \quad (12C)$$

The problem is solved by plotting and interpreting species distribution (Bjerrum) diagrams and titration curve diagrams for ions which influence pH (see Figure 19). These include sulphate, sulphide, fulvic acid, ammonia and inorganic carbon (Table 22). Figure 19a, plotted without H_2CO_3, shows that below pH 3.5, free H^+ is the most abundant species. Above pH 3.5, fulvic acid followed by H_2S are in the highest concentrations. Figure 19b shows a species diagram for fulvic acid (HFA), H_2S, and two alternative concentrations of C_T (10^{-5}M and 10^{-4}M). Figure 19c shows the titration curve corresponding to these concentrations. The equivalence points represent the start and end of an acidimetric titration (e.g., FA_1 represents the initial point and FA_2 represents the final point for fulvic acid). C_1 and C_2 are respectively the first and second equivalence point for an acidimetric titration of a 10^{-5}M C_T solution. Hence, in reverse, C_2 (the second equivalence point for 10^{-5} M C_T) represents the first titration point and C_1 (the first equivalence point for 10^{-5} M C_T) represents the final titration point for a bicarbonate alkalinity titration of a raindrop containing 10^{-5}M C_T. The titration curves are sketched from the starting point to the end point for each individual species; the composite curve for the water is not sketched, but would envelope the individual curves.

The species distribution diagrams (Figure 19b, c) allow the following observations:

(i) Fulvic acid requires the largest amount of base in the titration. Most of this base addition occurs over the pH range of 3.8 to 4.5.

(ii) Neither H_2S nor H_2CO_3* will have much effect upon the titration curve until the pH is greater than 5.

(iii) Below pH 3.7, free hydrogen ion would be the species requiring the largest amount of base.

(iv) For water containing 10^{-5}M C_T (i.e., water at equilibrium with the atmosphere) and 10^{-4} M sulphide, there are two regions of interest;

(a) between pH 5.5 - 6.5, both C_T and sulphide make roughly the same contribution to the titration curve and hence each will be equally important in influencing pH, and

FIGURE 19: DISTRIBUTION OF SOLUTE SPECIES AND TITRATION CURVES FOR OMBROTROPHIC PEAT BOG. SPECIES CONCENTRATIONS CONSIDERED: 10^{-4}M H_2S; $C_T = 10^{-5}$M; pFA = 3.55 (280 ueq/L HFA); SO_4^{2-} = 18 ueq/L (pS = 4.44), and NH_3 = 0.4 mg N/L (pNH_3 = 4.54)

FIGURE 19a: DISTRIBUTION DIAGRAM FOR HFA - FA^-; HSO^-_4 - SO_4^{2-}; H_2S - HS^- - S^{2-}; NH_4^+ - NH_3; H^+; OH^-; BUT WITHOUT C_T FOR pH RANGE 0.0 TO 14.0.

FIGURE 19b: DISTRIBUTION DIAGRAM FOR HFA - FA^-; H_SS - HS^-; $10^{-5}MH_2CO_3$ - HCO_3^- and 10^{-4}M H_2CO_3 - HCO_3^- for pH range 3.0 to 8.0.

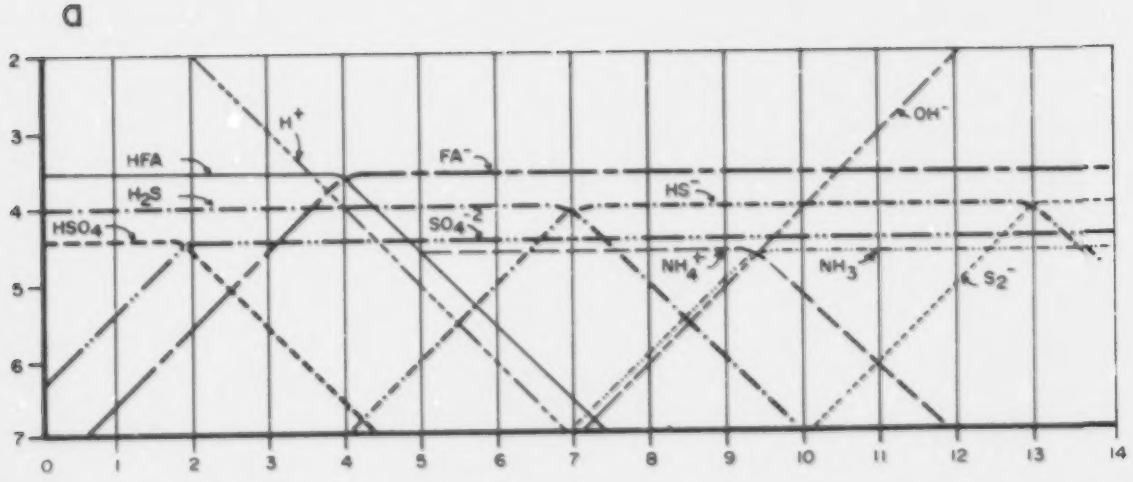
FIGURE 19c: SKETCH OF TITRATION CURVES FOR 280 uM HFA, 10^{-5}M C_T, 10^{-4}M $_2S$, and 10^{-4}M C_T for pH range 3.0 to 8.0.

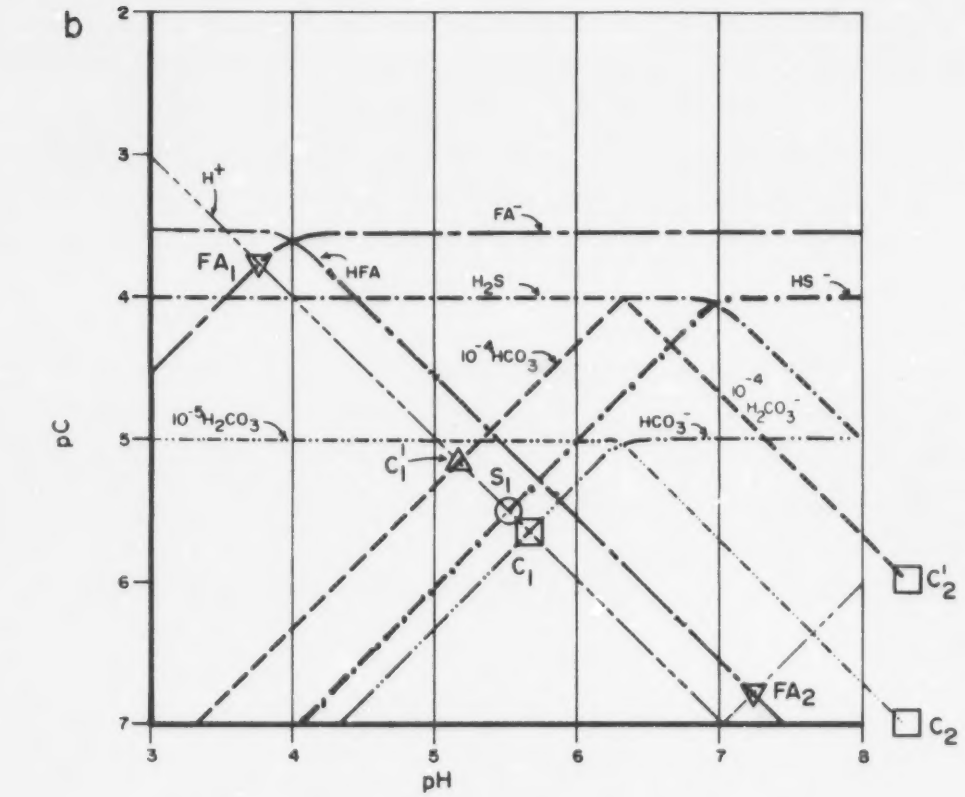
Definition of Terms for Figures 19b and 19c for Equivalence Point of Pure Solutions

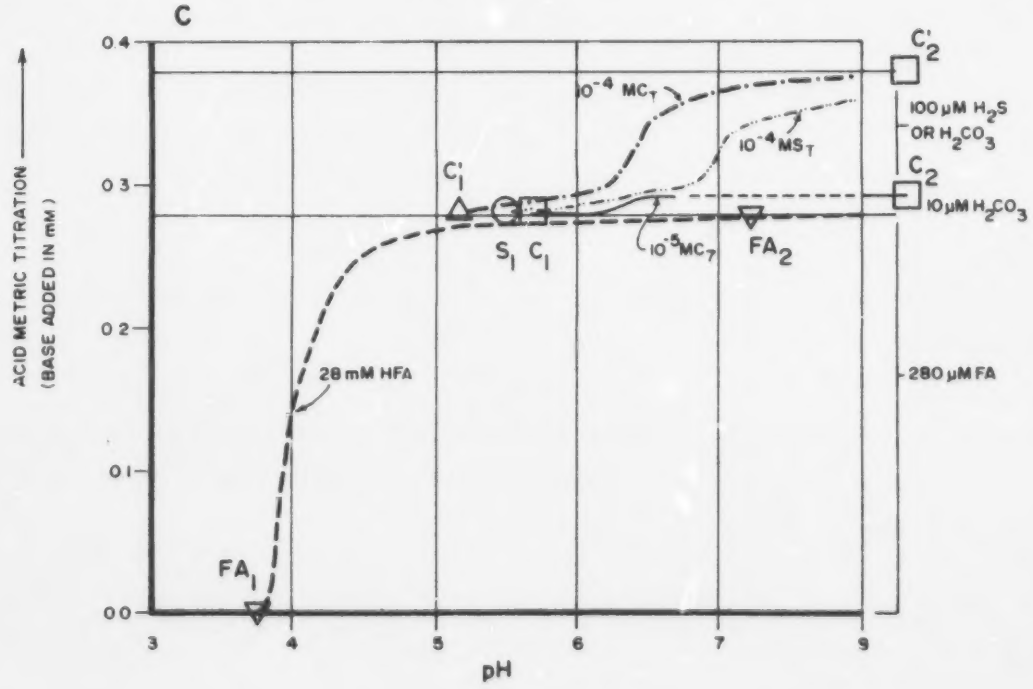
Symbol No.	Pure Solution	Symbol
(i)	HFA	FA_1
(ii)	NaFA	FA_2
(iii)	10^{-5}M H_2CO_3	C_1
(iv)	10^{-5}M Na HCO_3	C_2
(v)	10^{-4}M H_2CO_3	C_1
(vi)	10^{-4}M $NaHCO_3$	C_2
(vii)	10^{-4}M H_2S	S_1
(viii)	10^{-4}M NaHS	S_2 (not given because it occurs at pH = 10.0)

Data Used: H_2SO_4:pK_2 = 1.9; H_2CO_3*:pK_1 = 6.3, pK_2 = 10.3;
HFA:pK_1 = 4.0; H_2S:pK_1 = 7.0; pK_2 = 13.0;
NH_4^+:pK_1 = 9.3.

FIGURE **19** Distribution of Solute Species and Titration Curves for Ombrotrophic Peat Bog




b
pC
pH
H+
FA⁻
FA1
HFA
H2S
HS⁻
10⁻⁴HCO3⁻
10⁻⁴H2CO3
10⁻⁵H2CO3
HCO3⁻
C'1
S1
C1
C'2
C2
FA2


C
ACID METRIC TITRATION
(BASE ADDED IN mM)
pH
C'2
10⁻⁴ MCT
100 μM H2S
OR H2CO3
10⁻⁴MST
C'1
C2
10 μM H2CO3
S1 C1
10⁻⁵MC7
FA2
28 mM HFA
280 μM FA
FA1

(b) above pH 6.5, the sulphide system has the largest effect upon the titration curve and hence would be the largest influence on the pH.

(v) For water containing 10^{-4} M C_T and 10^{-4} M sulphide, C_T would have a slightly greater effect upon pH than sulphide between pH 5.2 - 5.7. The carbonate buffering system, C_T, would generally control pH for the range 5.7 - 7.5.

(vi) There is a narrow pH window between pH 3.7 - 4.5 in which fulvic acid buffers the system. Between pH 4.5 - 5.5, a rapid change in pH is expected from addition of a small amount of base. Hence, it will be quite difficult to accurately model pH in this region.

Thus, the following approximations for modelling pH in the generic ombrotrophic bog can be made:

(i) between pH 3.7 - 4.5, fulvic acid concentrations and electroneutrality can be used to model pH,

(ii) at pH $>$ 6.0, C_T and electroneutrality can be used to model pH, provided sulphide concentration is sufficiently lower than C_T; and

(iii) between pH 4.5 - 6.0, fulvic acid, C_T and electroneutrality can be used to model pH.

The following chemical procedure can be used to establish the validity of these approximations,

(i) a Gran titration (Stumm & Morgan, 1981) from the pH of the bog water (e.g., 4.0) to a pH of 3.5 by acid addition and then back to a pH of 8.3 by base addition,

(ii) concentration measurements for DOC, sulphide and sulphate,

(iii) inspection of the results from the Gran titration and the concentration measurements to establish if fulvic acid and inorganic carbon make the largest contribution to buffering capacity and control the pH in particular ranges.

For this model, electroneutrality is re-expressed in terms of the ANC (acid neutralizing capacity). It is defined as:

$$ANC = [HCO_3^-] + [2\,CO_3^{2-}] + [OH^-] + [FA^-] - [H^+] \text{ for the bog water} \quad (13A)$$

$$= [Na^+] + [K^+] + [2\,Mg^{2+}] + [2\,Ca^{2+}] - [2\,SO_4^{2-}] - [Cl^-] \quad (13B)$$

This allows retention of the definition of alkalinity (and acidity) as the equivalence point for $H_2CO_3^*$ - i.e., that,

$$Alk = [HCO_3^-] + [2\,CO_3^{2-}] + [OH^-] - [H^+]$$

For the approximation of Equation (13A), the expression for pH (H^+) is obtained from,

$$[H^+] = 1/2\left\{(ANC-K_1) \pm \sqrt{(ANC-K_1)^2 + 4K_1(ANC + FA_1)}\right\} \quad (14)$$

Here ANC is as defined in Equation (13B) and FA_T is the total fulvic acid concentration (FA_T = HFA + FA^-). The Gran titration can also be used to give estimates of ANC.

The overall model for pH then consists of Equation 14 for pH 3.5 and greater, and of Equation 11 for pH of 8.3 and less. Where, both fulvic acid and inorganic carbon are influential (e.g., pH 4.5 - 5.5), the two equations are spliced together. For both pH ranges, Alkalinity or ANC are modelled from concentrations of major cations and anions (Ca, Mg). Hence the appropriate metal models described in Section 9.5.1 are required as a part of the pH model.

In addition to equilibrium reactions in the water, the peat itself has three other properties which influence pH and are, in turn, influenced by pH (Section 3.3.3). They are:

(i) H^+ adsorbs to peat. At pH 7.2 approximately 80% of the available cation exchange sites on peat are occupied by H^+,

(ii) CEC increases with pH (Figure 20a), and

(iii) The apparent pK of organic acids in bog waters (i.e., for fulvic acid) varies as a function of pH (see Figure 20b).

The change in CEC with pH can conceptually be explained by approximately four different complexation sites which become operational over the pH range of 3-10. The four sites would have pKa's of approximately 4,6,8 and 10. An alternative explanation is that changes in the organic carbon molecule occurs which causes the effective pKa for one site to change with pH. This is the probable explanation for soluble organic carbon, and would involve two pKa's, one at 4.0 for carbonyl groups, and one at 9.0 for phenolic groups. Irrespective, of the mechanism, these variations should be modelled. They have been accounted for by Clymo (1967) through the relationship:

$$CEC = 0.3\ (pH-3) \qquad (15)$$

pKa can be calculated as a function of pH, based on a piece-wise linear relationship. For narrow ranges of pH, the values of CEC and pKa can be treated as constant. This approach is used for the diagnostic modelling results of Section 9.6.

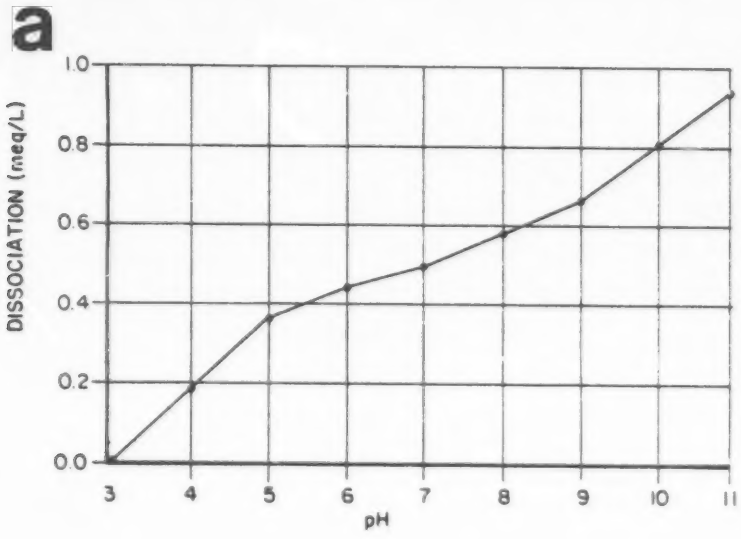
9.5.7. Conceptual Model for Oxygen and Redox Potential

The reduction of oxygen and other anions (e.g., NO_3^-, SO_4^{2-}) occurs because these elements act as final electron acceptors for bacterial respiration processes. The decay of organic carbon (matrix POC; soluble methane) is the energy source for respiration. The vertical sequence of processes mediate and define the redox potential from the atmospheric-water interface of the saturated zone through to strictly anaerobic waters.

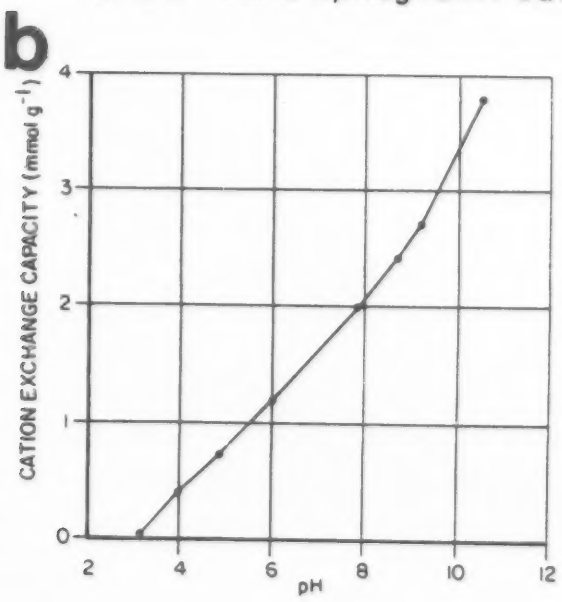
The metabolism of peat is complex. It involves:

- a supply of organics, (by production, sedimentation, consolidation) and oxygen (by diffusion)

FIGURE **20** Dissociation of Weak Acids in a Representative Sample of Bogwater. Background Electrolyte is 0.01 M NaCl.



Cation Exchange Capacity for Ba^{2+} for a Sphagnum Peat



- consumption of organics by bacteria for cellular metabolism and maintenance, and
- biochemical redox reactions induced by the decomposition of organics.

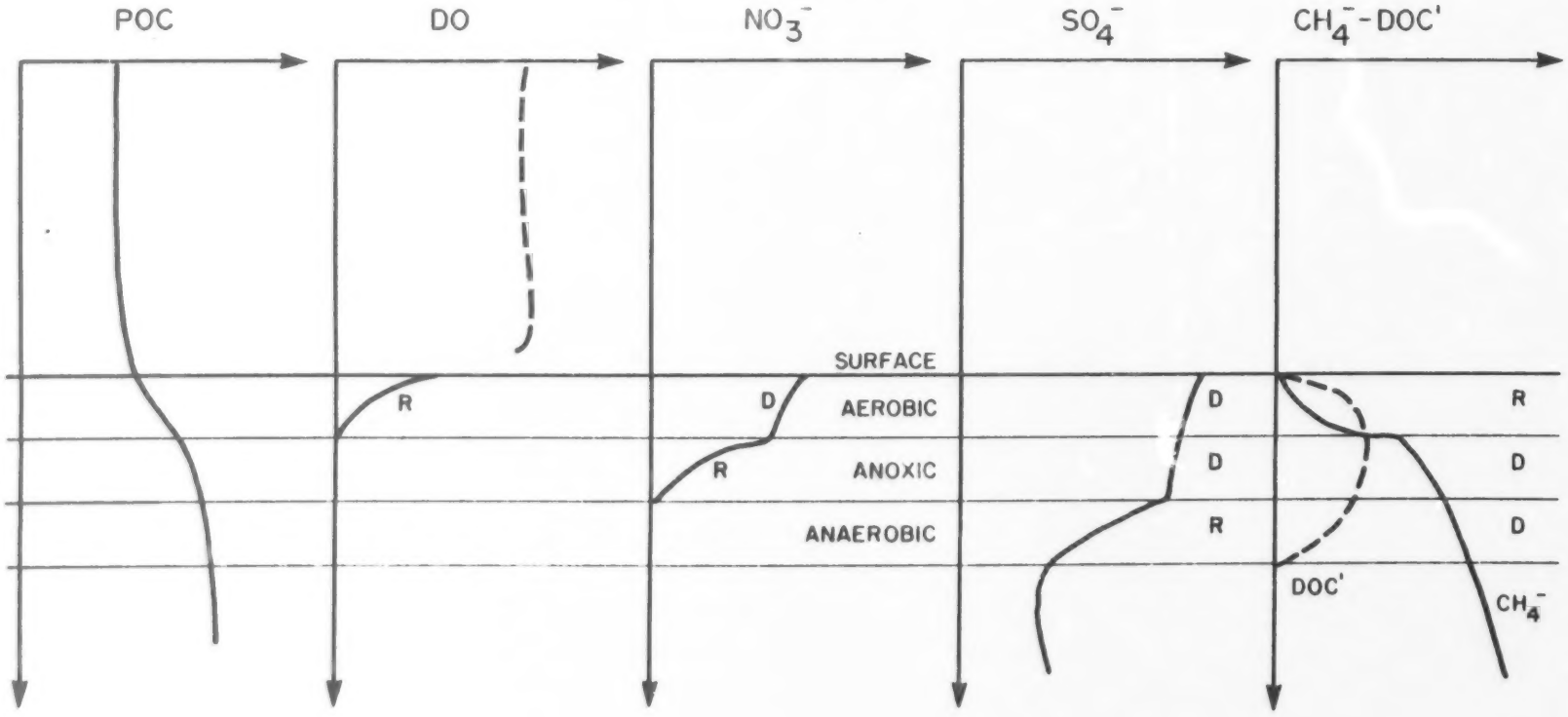
It may even involve polymerization of the organics to less biodegradable forms. At least four aqueous chemical species may be the final electron acceptors for metabolism: oxygen, sulphate, nitrate, and organic matter. Other aqueous species of potential importance include iron (Fe III) and manganese (Mn IV).

Equilibrium chemistry provides a reference point for considering the possible sequence of reactions in peat. In a system containing an excess amount of (i) organic matter, (ii) O_2, (iii) NO^-_3, (iv) SO^{2-}_4, (v) HCO^-_3, and (vi) oxides of iron (e.g., FeOOH(s)) and manganese (e.g., MnO_2(s)), oxidation of organic matter should first occur by reduction of O_2 (Stumm and Morgan, 1981). This would be followed by reduction of nitrate (denitrification or nitrate reduction), MnO_2, and then FeOOH(s). Finally fermentation of organic matter, and reduction of SO^{2-}_4 and CO_2 would occur. The reduction of nitrate and MnO_2 occurs at about the thermodynamic point in the sequence, as would the group of organic matter, SO^{2-}_4 and CO_2. The sequence of these reactions may occur vertically with depth, as the redox potential becomes increasingly negative, or in a horizontal fashion in local zones of lower redox potential.

A hypothetical sequence of profiles below the atmosphere-peat interface is given in Figure 21, for peat, dissolved oxygen (DO), nitrate, sulphate and dissolved organics (methane, and DOC). Oxygen concentration decreases with depth from the atmosphere-water interface to zero. Nitrate concentrations decrease primarily across the anoxic zone. Sulphate concentrations decrease in the top part of the anaerobic zone, do not decrease to zero in order to reflect field observations that certain bogs have sulphate deep in their anaerobic zones. Two soluble organic carbon species are shown; methane, one of the primary products of peat decomposition, and POC are the main cause of oxygen consumption in the aerobic zone; DOC^1, assumed to be an organic carbon by-product of peat decomposition in the aerobic zone, is the energy source for sulphate reduction. The depth to which DOC^1 diffuses is assumed to be the depth below which sulphate reduction ceases.

FIGURE 21

Sketch of Profiles of Substance Influencing Redox Potential in a Peat Bog
D= Zone in which it is expected that diffusion controls the profile
R= Zone in which reaction controls the profile



There are three substances whose production in the anaerobic zone will have some effect upon the redox sequence: H_2S, from matrix-S decay and SO_4^{2-} reduction; CH_4; and reduced metals, such as Fe^{2+}. Their production and subsequent diffusion through the aerobic zone represents an extra oxygen demand. Formation of MeS(s) as a precipitate decreases the actual transport of reduced species. In the model, it is assumed that diffusion and oxidation of these substances is small relative to that derived from methane and POC decay.

For oxygen, the resultant model (Klapwijk and Snodgrass, 1982) is:

$$\frac{d}{dt} COX - DOX; \qquad \frac{d^2}{dz^2} COX = ROX \tag{16A}$$

$$POD = \sqrt{2\, COX_o\, ROX\, DOX} \tag{16B}$$

$$ZOX = \sqrt{\frac{2\, DOX\, COX_o}{ROX}} \tag{16C}$$

where,
- COX is dissolved oxygen concentration at depth 'Z'
- COX_o is COX at Z=0 (g/m^3)
- DOX is the diffusion coefficient of oxygen (m^2/d)
- ROX is the consumption rate of oxygen ($g/m^3/d$)
- POD is peat oxygen demand (across the air-water interface) (g/m^2-d)
- ZOX is the thickness of the oxidized zone (m)
- Z is depth below the air-water interface
- t is time

For nitrate, the resultant model is (Klapwijk and Snodgrass, 1982

$$PND = (-RD - RN)\ ZOX + RD \sqrt{ZOX^2 \frac{RN + RD}{RN} + \frac{2\, CNO_3\, DW}{RD}} \tag{17A}$$

$$ZN = \sqrt{ZOX^2 \left(\frac{RN + RD}{RD}\right) + \frac{2\, CNO_3 DN}{RD}} \tag{17B}$$

Here,
- PND is the peat nitrate demand (g/m^2-d)
- RD is the rate of denitrification (g/m^3-d)
- RN is the rate of nitrification (g/m^3-d)

CNO_3 is nitrate concentration at air-water interface (g/m^3)

ZN is depth below water table of anoxic zone (m)

DN is diffusion coefficient for nitrate and ammonia (m^2/d)

The equation for nitrate includes the effects of nitrification in the aerobic zone; if ammonia production from aerobic and anoxic sources is sufficiently low, RN approaches zero, allowing simplification of these equations.

In these models, ZN is larger than ZOX; the thickness of the anoxic zone is ZN-ZOX. The values for DOX and DN are available in handbooks, provided that molecular diffusion dominates transport. The parameters RD, RN and ROX, are calibration parameters. Based upon arguments about bacterial energy sources,

$$ROX = \frac{20}{7} RD \tag{18}$$

For sulphate, a slightly different model evolves; because the bottom boundary does not necessarily approach zero as in the case for nitrates. It becomes

$$DSO_4 \quad \frac{d^2 [SO_4]}{d^2 z} = 0 \tag{19A}$$

$$B.C. \quad q_r [SO_4] - q_o [SO_4]_o = - D \frac{d[SO_4]}{dz} \tag{19B}$$

$$DSO_4 \frac{d^2 [SO_4]}{d^2 z} = RSO_4 \tag{19C}$$

A flux boundary condition is used at the lower boundary. RSO_4 is a calibration parameter. The subscripts 'a' and 'o' refer to atmospheric and air-water interface, respectively.

9.5.8 Effects of Oxygen Concentration, Temperature and pH upon Biochemical Parameters

Oxygen concentration primarily affects decay rate through its control of redox processes and nitrification. The observations of Foree and McCarty (1970) and Jewel and McCarty (1971) are used to calibrate relative decay rates.

pH is not known to have a significant effect on aerobic decay processes over the pH range of 4-8. However, it does affect nitrification rates and methanogenesis (i.e., decay rates under anaerobic conditions) at pH's less than 7 and 6, respectively.

Temperature causes an increase in respiration rates. Typically, decay rates double with a 10°C change in temperature. Using the Arrhenius activation energy concept,

$$\frac{K_T}{K_{20}} = \exp\left[\frac{-\Delta E}{2.3R}\left(\frac{1}{273+T} - \frac{1}{293}\right)\right] \qquad (21)$$

Where, K_T is the decay rate at temperature T
R is the gas constant
ΔE is activation energy
20 is 20°C

ΔE has values which range from 11 to 22 kcal/mol -°K (Klapwijk and Snodgrass, 1982) for decay processes.

In this work, the following expressions are adopted for pH and temperature effects upon nitrification (Halbert et al., 1980):

$$\text{Nitrification Rate} = \frac{k_{20} \exp\left[\frac{-19{,}970}{RT}\right]}{1 + \frac{10^{-pH}}{10^{-7}} + \frac{10^{-10}}{10^{-pH}}} \qquad (22A)$$

For anaerobic decay,

$$k = k_7 \left(\frac{10^{-pH} - 1}{10^{-5.5} - 10^{-pH}} \right)^{-1} \qquad (22B)$$

reasonably describes the effects of pH (Scharer, pers. comm.), where k is the coefficient for any pH, and k_7, is the rate at pH 7. For systems in which the pH variation occurs over a shallow thickness across the oxidized zone, these models are simplified to a constant decay rate for the aerobic zone and another decay rate for the anaerobic zone. The treatment of decay across the anaerobic zone is justified by the work of Clymo (1983) in which a first order decay model fit data for peat accumulated over several millenia.

9.6 Results of Calculations of Chemical Parameters

9.6.1 Chemical Processes in the Bog

Calculations of two processes in an undisturbed bog are presented: decay and pH (electroneutrality balances). Models for these two parameters are examples of 'assimilative models'. Input data are derived from literature sources. Where possible, comparisons of results to multiple data sets are made.

Decay Processes

Hemond (1980) provides data which allow for the examination of peat decomposition processes over a 200-year time scale (peat depth = 0.6 m). Pb-210 data were used to date the core. The only dichotomy (see Figure 22) is the calculated date of the 36-48 cm deep strata. The 12 cm strata above the 36-48 cm layer has an age calculated by Hemond of 28 years (see Table 24); the 12 cm strata below has an age of 61 years. Using the observed total stable Pb concentrations and these ages, the inferred bulk density of the peat is at variance with measurements (see Table 24). The bulk density is 65% too low, while that of the strata below is 34% too high. Assuming that the age of the bottom two strata is the same (37 years), the re-calculated bulk densities (respectively 0.039 and 0.044 g/cc) correspond more closely to the observed bulk densities.

TABLE 24: RECALCULATIONS OF AGE OF STRATA IN THOREAU'S BOG
(after Hemond, 1980)

Depth Increment (cm)	Hemond's Calculation T (yr)	Inferred Bulk Density	Observed Bulk Density	Recalculated Age
0-12	6	0.021	0.024	6
12-24	24	0.050	0.050	24
24-36	28	0.043	0.043	28
36-48	13	0.014 (.039)*	0.040	37
48-60	61	0.059 (.044)*	0.044	37

* Quantities in brackets correspond to 'recalculated age'.

A model which describes the peat profile shown in Figure 22 is (Clymo, 1983):

$$Y_t = \frac{P^o}{k}(1-e^{-kt}) \qquad (23)$$

where,

Y_t is the unit area quantity of peat (g/m^2) accumulated to time t

t is time

k is the decay rate

P^o is the rate at which peat enters the anaerobic zone.

Physically, this represents the peat accumulation rate minus the decay rate in the aerobic zone; hence, P^o is 'a net production rate'. Equation 23 is derived from the standard decay equation and its modifications:

$$\frac{d[POC]}{dt} = -k\,[POC] \qquad (7)$$

$$v_s \quad \frac{d[POC]}{dz} = -k[POC] \qquad (7A)$$

$$v_s \quad \frac{d[POC]\Delta z}{dz} = -k\,[POC]\Delta z \qquad (7B)$$

$$v_s \quad \frac{dP}{dz} = -k\,P \qquad (7C)$$

$$P = P^o \exp(-kz/v_s) \qquad (7D)$$

$$y_t = \int_o^t P\,dt \qquad (7E)$$

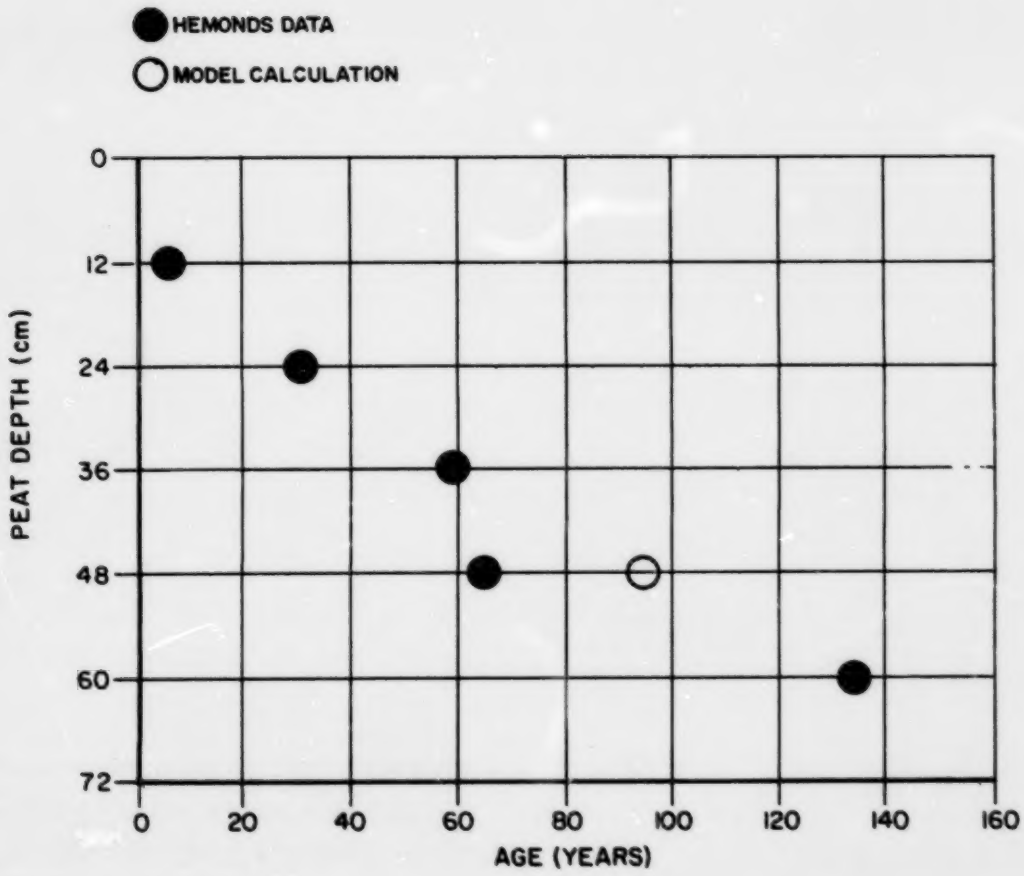
$$y_t = \frac{P^o}{k}\left[1-e^{-kt}\right] \qquad (7F)$$

The reformulation into t space (time of accumulation) from physical space is used because consolidation and compaction occur. This also changes the shape of the peat profile from one which follows a classical decay curve to one which increases with depth (see Figure 21).

Analyses of Hemond's data using Equation 23 give values for P^o of 340 g/m^2-yr and a decay constant (k) of 0.012 yr^{-1}. The mass which accumulates annually over the 0.6 m

FIGURE 22

Age of Peat in Thoreau's Bog



profile is 170 g/m^2-yr meaning that 170 g/m^2-yr is lost from the solid phase by decay processes in the 0.6 m column.

The rainfall-runoff balance and fulvic acid (FA) concentration in the surface water of Hemond's bog shows a loss of 240 meq/m^2-yr from the bog. Assuming a steady-state condition, and that Hemond's FA value is typical for bogs (10 meq/g TOC), this results in a production rate of FA in the bog of 24 g/m^2-yr.

In other more recent data, Hemond (pers. comm.) observed that the accumulation of CO_2 and CH_4 had a molar ratio of 1:2 under ice cover. The rate of accumulation was aproximately linear over time. The observed accumulation rates (CH_4:97 g C/m^2-yr; CO_2:140 g C/m^2-yr; total = 240 g C/m^2-yr) are 40% larger than those explainable from the peat profile. Because the peat profile is a better indicator of annual processes than short-term accumulation rates, it is assumed that the difference between FA export and peat decay is due to CH_4 and CO_2 production in the ratio of 1:2. This results in a calculated methane flux of 49 g/m^2-yr and a CO_2 flux of 97 g CO_2/m^2-yr. It provides model calibration data: decay processes become 14% FA, 29% CH_4 and 57% CO_2.

It is possible that the higher methane and CO_2 concentrations are real. They could result if the flux of POC entering the anaerobic zone is higher than that calculated from the POC profile. From the bulk density and Pb-210 dating, Hemond calculates that P^o is 480 g/m^2-yr, a value which is 40% larger than that calculated from the profile. A higher decay rate across the top 12 cm layer and P^o = 480 could represent the source of the higher CH_4/CO_2 fluxes; this source might not be picked up in a profile analysis. Transient aerobic conditions in the top 12 cm layer would provide for the higher decay rate. This line of reasoning does, however, not include transient changes in production rates and effects of temperature.

The soluble concentrations resulting from peat decay have been analyzed using steady-state analysis. Solution of the equation:

$$P = P^o e^{-kz/vs}$$

$$D\frac{d^2C}{dz^2} - v_o\frac{dC}{dz} + kP^o e^{-kz/vs} = 0$$

was obtained for the boundary condition:

1. At $Z = Z_i$, $-D \frac{dC}{dz} = 0$

2. At $Z = 0$, $D \frac{dC}{dz} + qr\, C^1 = qo\, C + v_o\, C$

Here: D is the diffusion coefficient (0.0073 m^2/yr)
v_s the sedimentation velocity (0.0046 m/yr)
v_o the pore water velocity (0.0046 m/yr)
qr the annual rainfall (1.42 m/yr)
qo the runoff rate (0.24 m/yr)
C^1 the rainfall concentration
Z_i the thickness of the peat layer (0.6 m)

The frame of reference (Z = 0) is the surface of Hemond's bog. This equation assumes that compaction is minimal. Hence, it is an idealization of an actual peat system. It assumes that only vertical water flow and diffusion affect pore water concentrations.

Calculated concentrations at the saturated zone and at the bottom of the 0.6 m section (135 years old) are given in Table 25 for fulvic acid and total carbon concentrations in pore water. The standard conditions are for molecular diffusion and a pore water velocity equal to the peat accumulation rate (0.0046 m/yr). The next two conditions represent higher pore water velocities. A velocity of 0.07 m/yr represents the order of magnitude of infiltration rates in sandstones with a vertical piezometric gradient of 1% (see Section 9.4). The last condition of Table 25 represents a diffusion coefficient which is ten times that of standard.

The calculated concentrations for the highest velocity condition substantially reduce concentrations throughout the peat column compared to standard conditions. The higher diffusion coefficient lowers the concentration at the bottom of the column while increasing the concentration at the top of the column. None of the calculations give the observed FA concentrations of 30-40 mg/L TOC at the bottom of the peat column. There are several explanations:

TABLE 25: CALCULATED SOLUBLE CARBON CONCENTRATIONS IN PORE WATER (mg/L)

Condition for Calculation	Surface of Peat Section		Bottom of Peat Section	
	Fulvic Acid	Total Carbon	Fulvic Acid	Total Carbon
Standard (Coefficients given in text)	120	880	1100	8100
Standard except $V0 = 0.0091$ m/yr	110	760	-	-
Standard except $VO = 0.07$ m/yr	28	200	430	3100
Standard except $VO = 0.073$ m^2/yr	200	1400	400	2900

- o decay rates decrease substantially towards the bottom of the column; this explanation is not too plausible given the ability of the peat decay model to fit the particle data;
- o consolidation causes the model to overpredict concentrations in lower layers; this is erroneous reasoning because consolidation increases bulk density and hence decay flux in the lower strata;
- o the rates of vertical transport are higher than those given in Table 25;
- o horizontal transport occurs throughout the peat column; and
- o the rate of production of fulvic acid decreases throughout the column, while most of methane and CO_2 produced by decay is volatilized.

The last two reasons are the most plausible, but lack of methane and CO_2 data preclude verification of the last explanation.

The calculated methane flux can be checked by comparison with other data. No flux data for bogs were found. However, for Hamilton Harbor, an embayment subjected to large standing crops of algae, gaseous methane fluxes of 21 g/m^2-yr from the sediments have been measured (temperature 8°C) (Snodgrass, 1979).

Assuming that the methane flux causes oxygen consumption at the atmosphere-water interface, the POD model (Equation 16) can be used to calculate the thickness of the oxidized zone. For Hemond's bog, sulphate reduction would consume 0.8 g C/m^2-yr. This is small compared to the calculated methane flux (49 g C/m^2-yr). If we assume that 100% or 2% of the methane flux may be consumed by oxygen processes at the air-water interface, the thickness of the oxidized zone is calculated to be of the order of 0.4-4 mm and 2-20 cm, respectively (Table 26). The 2% value is arbitrarily chosen to represent conditions where volatilization is the main mechanism for removal of methane from the bog. This analysis ignores the influence of peat decay upon oxygen consumption. It suggests that the thickness of the oxidized zone may be measureable using careful sampling techniques, but that it is expected to be small provided that diffusivity type processes have 'molecular' scales.

Electroneutrality Balances and Bog pH

The data of Table 22 permit evaluation of the electroneutrality condition and bog pH, but presents problems because it is a generic data set. Gorham et al. (1984) present a set of

TABLE 26: THICKNESS OF OXIDIZED ZONE (ZOX) FOR VARIOUS CONDITIONS

Portion of Methane Flux Consumed	ZOX FOR $D = 0.0073\ m^2/yr$	ZOX FOR $D = 0.073\ m^2/yr$
100 %	0.4 mm	4 mm
2 %	2 cm	20 cm

data derived from bogs in eastern North America on a transect running from Manitoba through Ontario and Quebec into Newfoundland. The cation charge (Ca, Mg, K, Na, H) is 258 ueq/L and the anion charge (SO_4, Cl) is 118 ueq/L, leaving an anion deficit of 140 ueq/L attributed to fulvic acid. For the mean DOC concentration of 29 mg/L, this corresponds to an organic carbon capacity of 4.8 meq/g TOC on the fulvic acid. This capacity is much lower than that observed for other environments where values are typically 10-15 meq/g TOC.

Gorham's data can, however, be analyzed in a slightly different fashion from that presented in his publication. Assuming that pH is controlled by the fulvic acid system according to the reaction,

$$HFA \rightleftharpoons H^+ + FA^-$$

and that the pH corresponds to the pK of the reaction, the H^+ concentration of 93 ueq/L corresponds to a pH and pK of 4.03. This pH (4.03) is typical of bogs (see Table 17). For this condition,

$$[HFA] = [FA^-]$$

and hence the total capacity of the fulvic acid is 2 x 4.8 = 9.7 meq/g C.

Gorham's data does not include other metals and anions observed in bog waters. For the data of Table 22, inclusion of Al^{3+}, Fe^{2+}, Mn^{2+}, Cu^{2+}, Hg^{2+}, Pb^{2+} and NH_4^+ gives an additional cation charge equivalent of 174 ueq/L for a total of 432 ueq/L. Most of this charge is due to Al^{3+} and Fe^{2+}. The aluminum data of Table 22 are typical of the literature. Schnitzer (1984) argues that fulvic acids are condensation products of smaller molecules held together by hydrogen bonding, and that metals are adsorbed onto these organic molecules. The ratio of Al/TOC in Table 22 is 0.038 mg Al/mg TOC while that of organics carried through a lake in New Hampshire is 0.055 mg Al/mg TOC. If the organics of these systems have similar properties, it is probable that most of the pore water aluminum described in Table 22 is in the form of an organic-Al complex.

The additional anions ($H_2PO_4^-$, S^{2-}, AsO_4^{3-}, SiO_2, NO_3^-) increase the net anion charge by 9 ueq/L to a total of 127 ueq/L. This assumes that silica is in the H_4SiO_4 form. The

cation-anion deficit, 306 ueq/L, gives a fulvic acid capacity of 10.5 meq/g TOC, a concentration typical of literature values for other systems.

But this value presents a dichotomy for the combined data set. For the electroneutrality model:

$$ANC = [H^+] + [FA^-]$$

ANC = 399 ueq/L, $[H^+]$ = 93 ueq/L and $[FA^-]$ = 306 ueq/L, resulting in a fulvic acid capacity of 21 meq/g TOC, a value much larger than typically observed. However, if the FA^-/HFA ratio is assumed to be 5:1, the pK is 3.33 and the fulvic acid capacity is 12.7 ueq/L. If the ratio is assumed to be 3:1, the pK is 3.6 and the fulvic and capacity is 17 ueq/L. Such values for pK and fulvic acid capacity are plausible, but probably out of the range of typical bog waters.

Given the present data set, these different explanations cannot be resolved. It is plausible that Gorham's data set does not have significant quantities of aluminum and iron, the main ions contributing to the additional cation-anion imbalance. For such conditions, the pK of 4.03 and fulvic acid capacity of 9.7 meq/g TOC with pH = pK is reasonable. For other bog waters, it is possible that:

- they do not fit the typical data observed for soils and surface waters,
- other cations (Ca, Mg, Na) are lower, or
- other anion concentrations are higher.

The pK's for fulvic acids can range over two orders of magnitude (say pK = 3.5 to 5.5) over the pH range of 3 to 6 due to charge interactions between bonds involving C = 0 and C-0H on carboxyl groups and between adjacent groups. Hence, slightly different behaviour may occur for different bogs.

To model pH, 280 ueq/L of HFA with a pK of 4.03 is assumed. The Bjerrum diagrams (species distribution of concentration versus pH) for HFA-FA^- and other species are given in Figure 19 (see Section 9.5.6). Their description and derivation suggest that FA, C_T and perhaps sulphide, are required to model the H^+ concentration of bogs over the range 3.5 to 7. But over this range, exchange of H^+ with peat particles must also be

considered. This can be analyzed by comparisons of the mass of H^+ in different organic reservoirs. Calculations involving mass balances for H^+ are given in Table 27. The values for adsorbed forms are based upon measurements which suggest CEC values of 170 meq/100 g of peat at pH 7.2 of which 120 meq is due to H^+. The adsorbed values for pH 4 are inferred from the relationship given in Figure 21b. For DOC, the capacity of 10 meq/g of carbon and DOC concentration of 29 mg TOC/L are used at pH 4. For pH 7.2, the capacity is inferred from Figure 16 which suggests an increase of 2.5 times this capacity from pH 4 to 7.

At both pH 4 and 7, the calculations of Table 27 indicate that adsorption represents the largest pool of H^+ while DOC is the second largest pool. If carbonate concentration increases as pH increases from 4 to 7, then H_2CO_3-HCO_3 is the second largest pool at pH 7. Hence, if DOC or inorganic carbon is the buffering system controlling the pH, then adsorption (cation exchange) must be viewed as a process which does not make a substantial contribution to buffering systems controlling the pH over narrow ranges. Alternatively, it may be a reservoir which undergoes biochemical reactions which do not interact significantly with buffering systems or a reservoir whose release/uptake of H^+ is readily neutralized by the dominant buffering systems such as HFA or H_2C0_3. The recent evidence of S. Bayley (pers. comm.) with respect to the effects of acid irrigation upon pH suggests some influence of H^+ exchange upon pH in the runoff waters.

9.6.2 Simulation of the Chemistry of Mine Discharge Waters; Dry Mining Scenario

For these calculations, it is assumed that the water table is drawn down 25 cm due to ditching and that this area is exposed to rainfall, and becomes aerobic. Calculations of leachate concentrations are for steady-state conditions and constant flow. Input values are based, where possible, on literature values, or on plausible ranges for those parameters for which no published data exist.

pH

The chemical parameters controlling pH are ANC (acid neutralizing capacity) and fulvic acid concentration.

TABLE 27: TOTAL H^+ PER LITRE IN DIFFERENT FORMS WHICH CAN BE EXCHANGED OVER THE pH RANGE 3 - 8

	Total H per Litre	
	pH = 4.0	pH = 7.2
Adsorbed	2.4 meq/L	20 meq/L
DOC	0.29 (10 meq/g; 29 mg/L)	0.73
H_2S	0.20	0.15
H_4SiO_4	0.33	0.33
H_2PO_4	0.006	0.006
H^+	0.1	10^{-4}
NH_4^+	0.03	0.03
HCO_3^-	.02	.01-2

Gorham et al.'s (1984) data are used as input values (Table 28 - compare to Table 22). The ANC is 47 ueq/L and the fulvic acid concentration is 29 mg/L with an assumed FA concentration of 10 meq/g TOC. These values give a calculated pH (according to Equations 13B and 14) of 4.0, in agreement with the observed pH (4.03).

For aerobic conditions, assuming that the decay rate remains the same as the long-term rate (0.012%/year), that fulvic acid remains a constant 14% of POC decay and that peat carbon concentration is 4.4×10^6 mg/m^3 (see Table 22), the resultant fulvic acid concentration is 7.5 mg/L as TOC. If the decay rate remains constant, but fulvic acid production decreases under aerobic conditions, the resultant fulvic acid concentration decreases.

Calculated pH's in the bog outflow are given for three fulvic acid concentrations (7.5, 5, 1 mg/L) and two ANC conditions. The ANC conditions are based upon ammonia produced by decay processes either:

- remaining as ammonia in the outflow waters, or
- being nitrified to nitrate.

The value for ammonia in Table 28 is the concentration due to decay of particulate nitrogen at the long-term anaerobic decay rate (0.012%/year) mediated by the volume of outflow. Cation (Na, K, Ca, Mg) concentrations in the outflow (Water 2) are the same as the bog waters (Water 1) of Gorham et al. (1984), because it is assumed that adsorption maintains the same concentrations in the runoff. Anion concentrations (Water 2) are the same as those of rainfall and are based upon the modelling assumption that none of the anions adsorb significantly. Furthermore, calculations assume that sulphate in runoff waters is not reduced.

If the ammonia produced by decay is nitrified, the calculations (Table 28) suggest that pH will remain at approximately 4.0 for fulvic acid concentrations of 7.5 mg/L and lower. That is, fulvic acid buffering explains the pH. But if ammonia is not nitrified, the calculations suggest that pH increases substantially. In these cases, the model (Equations 13B, 14) is inadequate and the influence of C_T upon pH must be considered.

TABLE 28: CALCULATED pH FOR DRAINAGE WATER FROM DRY MINING

(a) Calculation pH

Bog Condition		Special Conditions	Calculated pH
Undisturbed Bog		FA_1 = 290 mg/L; water 1	4.0
Dry Mining	(a)	NH_4^+L FA_T = 7.5 mg/L; Water 2	4.7
	(b)	NO_3^-; FA_T = 7.5 mg/L; Water 2	4.02
	(c)	NH_4^+; FA_T = 5 mg/L; Water 2	5.5
	(d)	NO_3^-; FA_T = 5 mg/L; Water 2	4.03
	(e)	NH_4^+; FA_T = 1 mg/L; Water 2	undefined
	(f)	NO_3^-; FA_T = 1 mg/L; Water 2	4.04

b) Composition of Waters

Parameter	Concentration in Water Bog (ueq/L)	Concentration in Rainfall (ueq/L)	Concentration in Water 1 (NH_4^+ Present) (ueq/L)	Concentration in Water 2 (NO_3^- Present) (ueq/L)
Na^+	96 ueq/L	6.5	96	96
K^+	5.2	2.3	.2	5.2
Ca^{2+}	27	41	27	27
Mg^{2+}	37	6.6	37	37
NH_4^-	-	18	45	0
H^+	93 (pH = 4.03)	89 (pH = 4.05)	TBC	TBC
SO_4^{2-}	18	103	103	103
NO_3^-	-	47	47	92
Cl^-	100	13	13	13
ANC	47.2	-89	47	-43

TBC - To be calculated.

Nutrients and Metals

Analysis of the models for nutrients (C, N, P) and metals (Fe, Al, Mn, Cu, Zn, Hg, Pb) show that two critical parameters affect metal transport from the bog:

- for Fe and Al, the rate of desorption from the peat and the amount of metal complexed with soluble fulvic acids; and
- for Mn, Cu, Zn, Hg and Pb, the rate of dissolution of the metal sulphide and the amount of metal complexed with fulvic acid.

The critical parameter affecting FA, N and P transport is the rate of decay of matrix peat. All parameters are affected by the hydrological pathway and the runoff rate.

Calculations of nutrient and metal export are given in Table 29 for nutrients and metals for two different assumptions: the decay rate is 1%/day or it is 1%/year. The lower rate (1%/year) is similar to the decay rate of peat under anaerobic conditions. The upper rate is a value which is typically at the lower end of the range of values observed for the decay of organics in rivers. This range (1%/day - 1%/year) bounds the range found in our cursory review of precipitation - dissolution kinetic literature. For example, laboratory and lysimeter studies suggest pyrite oxidation rates which vary from 5%/year to 0.5%/year. For calcite, recent studies give rate constants on the order of 1-10%/year for 1 cm particles and 1-10%/day for 1 micron particles (Plummer et al., 1978; Dregbrodt, 1981).

Nutrients

Fulvic acid concentrations are calculated to be of the order of 7.5 mg/L. Concentrations for ammonia (or nitrate) are 0.6 mg/L, while those for total phosphorus are 20 ug/L. This assumes a peat decay rate of 1%/year. The calculated concentrations are of the order of or in excess of the water quality guidelines given in Table 20.

Metals

Calculated concentrations for iron and aluminum released by desorption vary from 25-50 ug/L for a release rate of 1%/year to 9-20 mg/L for a release rate of 1%/day. The higher

TABLE 29: CALCULATIONS OF NUTRIENT AND METAL CONCENTRATIONS IN BOG OUTFLOW FOR DRY MINING

Parameter	Assumed Phase	Calculated Concentration for Decay Rates of		Guidelines
		1%/d	1%/yr	
FA_T	Peat (POC)	-	7.5 mg/L	
N	Peat (PN)	-	0.6 mg/L	20 ug/L (NH_3)
Tp	Peat (PP)	-	20 ug/L	
Fe	Adsorbed	20 mg/L	50 ug/L	300 ug/L
Al	Adsorbed	9 mg/L	25 ug/L	
Mn	Sulphide	2 mg/L	4 ug/L	
Cu	Sulphide	0.2 mg/L	0.6 ug/L	5 ug/L
Zn	Sulphide	0.7 mg/L	2 ug/L	30 ug/L
Hg	Sulphide	2 ug/L	.006	0.2 ug/L
Pb	Sulphide	0.6 mg/L	2 ug/L	5 ug/L

concentrations are at a level where a metal hydroxide precipitate might form at pH 4.0, but the formation of a metal organic complex precludes such precipitation. Water quality guidelines are at a level between the calculated concentrations for iron.

Results are similar for Mn, Cu, Zn, Hg and Pb, released by dissolution of their sulphide minerals. The lower concentration is of the order of 1 ug/L whereas the higher concentration is of the order of 1 mg/L for all metals. These calculated concentrations bracket guidelines (see Table 29). The calculated mercury concentrations are quite low because the peat mercury concentrations given in Table 22 are quite low. These concentrations, abstracted from Table 16, may be low for many peat bogs.

Toxicity

At present, water quality objectives are formulated in terms of total metal concentrations (Table 20). This is done for a variety of reasons including technological inability to measure all of the metal species concerned. Recently, evidence has accumulated which suggests that it is the ionic metal concentration which is toxic to biota not the total metal concentration. In the following discussion, the toxicity of copper to algae is evaluated using the modelling concepts described above.

For the complexation reaction:

$$Cu^{2+} + FA^{-} \rightleftharpoons CuFA^{+} \qquad K = 10^{8.9}$$

the ionic concentration is $\left[Cu^{2+}\right]$ whereas the total concentration is $\left(\left[Cu^{2+}\right] + \left[CuFA^{+}\right]\right)$. For 0.2 mg/L total Cu concentration in the effluent stream, the modelling calculations give:

$$pCu_T = 5.4$$

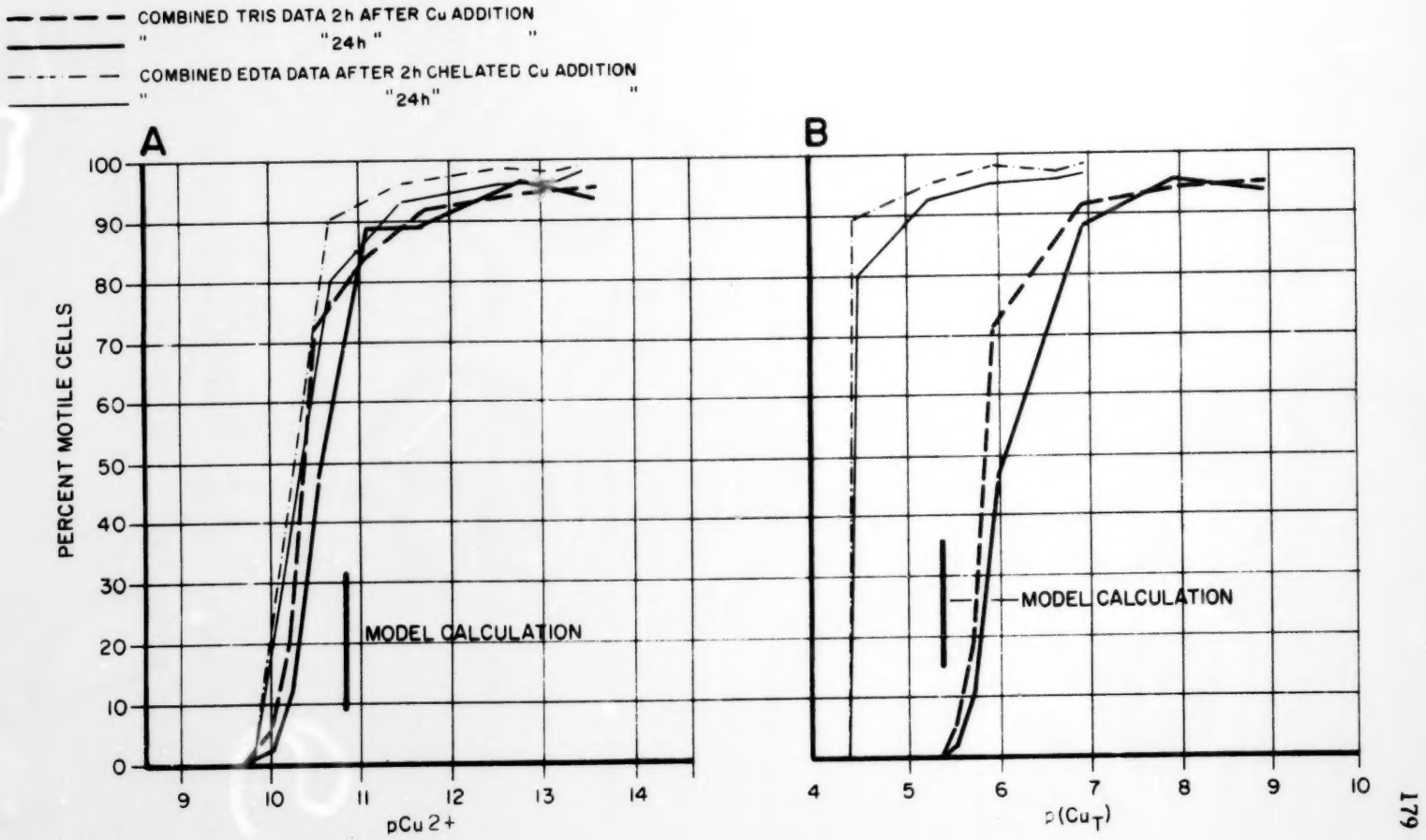
and a value for

$$Cu^{2+} \text{ of } pCu^{2+} = 10.8$$

Here, the symbol "p" before the symbol Cu represents $-\log \left[Cu\right]$, analogous to the definition for pH ($= -\log \left[H^{+}\right]$).

FIGURE 23

Motility vs. pCu^{2+} and pCu_T



The data of Anderson and Morel (1978) provide a reference point for these calculations. In controlled laboratory conditions, they evaluated the toxicity of copper to algal cells over a range of copper concentrations. These data are summarized in Figure 23. The percentage of motile cells are plotted versus pCu^{2+} and pCu_T. Motile cells are those which are healthy and uninhibited by copper. For both diagrams, one can give the following interpretation: as the pCu^{2+} (or pCu_T) increases (i.e., $[Cu^{2+}]$ or $[Cu_T]$ decreases), the percentage of motile cells increases from 0% to 100% at a certain threshold concentration. In one solution (Tris), the threshold concentration is $pCu_T = 4.3$, while in a second solution containing a strong complexing agent (EDTA), the threshold concentration is much lower ($pCu_T = 5.7$).

These results, at first, might appear to be confusing - for the same algal cells, two different total copper concentrations, one and one-half orders of magnitude apart, cause toxicity problems. However, because of the well defined solutions used in the study, one can calculate the Cu^{2+} concentration (the concentrations are so low that one cannot reliably measure $[Cu^{2+}]$ at these levels). When the calculations are made (Figure 23a), the data exhibit one threshold value - copper is harmful to the algae at the level of $pCu^{2+} = 10.3$ for both solutions. This evidence suggests that Cu^{2+} rather than Cu_T should be used as the parameter for assessing metal toxicity to algae.

The model calculations for total copper concentration are also displayed in Figure 23b. With respect to total copper concentrations, the graph suggests that copper is harmful to the algae of the TRIS solution, but not to algae in EDTA solution. But the calculated concentrations for Cu^{2+} are lower than the threshold for both the TRIS and EDTA solutions (see Figure 23a) suggesting that Cu_T concentration (0.2 mg/L) in the presence of fulvic acid would not be harmful to algae, although it exceeds water quality guidelines by two orders of magnitude.

The extent to which the model's calculations can be used to estimate toxicity will continue to be evaluated. Further definition of equilibrium conditions complexation constants and the nature of the fulvic acid (or humic substances more generally) are required.

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